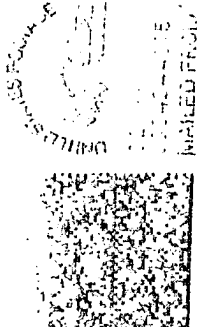


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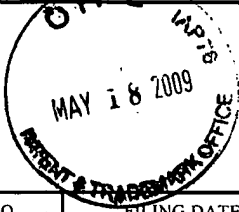
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/533,920	06/07/2005	Carl Towns	14113-00039	2378
23416 7590 05/13/2009 CONNOLLY BOVE LODGE & HUTZ, LLP P O BOX 2207 WILMINGTON, DE 19899			EXAMINER YAMNITZKY, MARIE ROSE	
			ART UNIT 1794	PAPER NUMBER
			MAIL DATE 05/13/2009	DELIVERY MODE PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary**Application No.**

10/533,920

Applicant(s)

TOWNS ET AL.

Examiner

Marie R. Yamnitzky

Art Unit

1794

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 04 March 2009.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1-24 is/are pending in the application.
- 4a) Of the above claim(s) 10-13 and 15-24 is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 1-9 and 14 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
 2. ☐ Certified copies of the priority documents have been received in Application No. _____.
 3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- * See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|--|---|
| 1) <input checked="" type="checkbox"/> Notice of References Cited (PTO-892) | 4) <input type="checkbox"/> Interview Summary (PTO-413) |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) | Paper No(s)/Mail Date. _____ |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO/SB/08) | 5) <input type="checkbox"/> Notice of Informal Patent Application |
| Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____ |

1. Applicant's election with traverse of Group I, claims 1-9, in the reply filed on March 04, 2009 is acknowledged. The traversal is on the ground(s) that all the claims have been previously examined by the examiner and therefore there is no undue burden on the examiner. This is not found persuasive because the examiner to whom the application is presently assigned is not the examiner who examined the claims prior to the restriction requirement mailed February 06, 2009 and, as correctly noted in applicant's response filed January 22, 2009, the indenofluorene structure of the previously applied prior art of Becker et al. is not the same as applicant's formula (I) structure. The Becker et al. reference was relied upon for each of the prior art rejections set forth in the final rejection mailed October 22, 2008; those rejections have been withdrawn and prosecution re-opened. Accordingly, the present examiner needs to begin the examination process as if the claims had not previously been examined.

The claims lack unity of invention for the reasons set forth in the restriction requirement mailed February 06, 2009. The requirement is still deemed proper and is therefore made FINAL. However, given the teachings of the prior art applied in this action, the examiner withdraws the requirement for restriction between Group I (claims 1-9) and Group IV (claim 14).

2. Claims 10-13 and 15-24 are withdrawn from further consideration pursuant to 37 CFR 1.142(b), as being drawn to nonelected inventions, there being no allowable generic or linking claim. Applicant timely traversed the restriction (election) requirement in the reply filed on March 04, 2009. See MPEP 821.04, 821.04(a) and 821.04(b) regarding rejoinder. Note that

even if present claims 1-9 and 14 were determined to be allowable without further amendment, some of the withdrawn claims do not currently meet the conditions for rejoinder.

3. Claims 1-9 and 14 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Clarification is required regarding the “optionally substituted” language set forth in line 1 of claim 1. The repeat units of formula (I) have four variables, R_1 - R_4 , at least one of which must comprise an aryl or heteroaryl group. It is not clear if the “optionally substituted” language:

(a) pertains to R_1 - R_4 and means essentially the same thing as the requirement that at least one of R_1 - R_4 comprises an aryl or heteroaryl group; or

(b) pertains to R_1 - R_4 and means that the possibilities recited for R_1 - R_4 may be further substituted (e.g. an alkyl group may be a substituted alkyl group); or

(c) does not pertain to R_1 - R_4 and means that the unit of formula (I) may be substituted at positions in addition to R_1 - R_4 .

4. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

(e) the invention was described in (1) an application for patent, published under section 122(b), by another filed in the United States before the invention by the applicant for patent or (2) a patent granted on an application for patent by another filed in the United States before the invention by the applicant for patent, except that an international application filed under the treaty defined in section 351(a) shall have the effects for purposes of this subsection of an application filed in the United States only if the international application designated the United States and was published under Article 21(2) of such treaty in the English language.

5. Claims 1, 2, 8 and 14 are rejected under 35 U.S.C. 102(b) as being anticipated by Peng et al. in *Acta Polymerica*, Vol. 49, pp. 244-247 (1998).

See the entire article. Peng's polymers, which are disclosed for use in an organic light emitting device, are polymers comprising a repeat unit of present formula (I) wherein one of R₁ and R₂ is an aryl group and the other is hydrogen, one of R₃ and R₄ is an aryl group and the other is hydrogen, and the polymer further comprises a second repeat unit, thus anticipating a polymer per present claims 1, 2 and 8, and an organic light emitting device per present claim 14.

The examiner notes that the present claims do not explicitly limit how the repeat unit of formula (I) is incorporated into the polymer chain. The orientation of the unit as shown in Scheme 1 of the prior art is not outside the scope of the present polymer claims.

6. Claims 1-4, 8, 9 and 14 are rejected under 35 U.S.C. 102(e) as being anticipated by Frey et al. (WO 02/095841 A2).

See the entire document. In particular, see page 9, lines 1-5, formula (IX) on page 9, p. 11, l. 1-14, and p. 13, l. 7-13.

Frey's conjugated unit of formula (IX) encompasses the repeat unit of present formula (I). While Frey et al. do not provide a specific example of a polymer comprising a repeat unit of present formula (I), it is the examiner's position that given Frey's disclosure, one of ordinary

skill in the art at the time of the invention could at once envisage homopolymers and copolymers within Frey's disclosure comprising a repeating unit of Frey's formula (IX) wherein each of Z^2 and Z^3 is $C(R^4)(R^5)$ and one or both of R^4 and R^5 is an aryl, aryloxy or arylalkyl group (any of which meets the present claim requirement of an R group that comprises an aryl group). With respect to present claims 8 and 9, Frey et al. teach copolymers, and it is the examiner's position that one of ordinary skill in the art at the time of the invention could at once envisage copolymers comprising repeat units of present formula (I) and triarylamine repeat units given Frey's disclosure of units of formulae (IX)-(XII). Frey's formula (IX) encompasses units of present formula (I), and each of Frey's formulae (X)-(XII) represents a triarylamine repeat unit.

7. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

8. Claims 1-9 and 14 are rejected under 35 U.S.C. 103(a) as being unpatentable over Frey et al. (WO 02/095841 A2) as applied to claims 1-4, 8, 9 and 14 above, and further in view of Hu et al. (US 6,479,172 B2).

Frey's disclosure encompasses polymers within the scope of present claims 1-9 and an organic light emitting device comprising such a polymer as per present claim 14. Frey et al. do not, however, provide a specific example of a polymer within the scope of the present claims. It

is the examiner's position that some polymers within the scope of present claims 1-4, 8 and 9 could have been at once envisaged by one of ordinary skill in the art at the time of the invention given Frey's disclosure.

In the alternative, polymers within the scope of present claims 1-4, 8 and 9, and well as polymers within the scope of present claims 5-7, would have been obvious to one of ordinary skill in the art at the time of the invention given Frey's disclosure, and given the disclosure of Hu et al. which demonstrates that compounds having an indenofluorene structure substituted on the fluorene rings were useful as light-emitting compounds for an organic light emitting device. For example, see column 39, line 41-c. 51, l. 57 of the patent to Hu et al. It would have been obvious to one of ordinary skill in the art at the time of the invention to make homopolymers and copolymers having units of Frey's formula (IX). It would have been within the level of ordinary skill of a worker in the art at the time of the invention to make various homopolymers and copolymers having units of Frey's formula (IX) and to select specific possibilities for the variables of formula (IX) from those taught by Frey et al. Based on the disclosure of Hu et al., one of ordinary skill in the art at the time of the invention would have reasonably expected that homopolymers and copolymers of Frey's formula (IX) wherein the Z variables are selected so as to provide alkyl and/or aryl substituted indenofluorene units would provide light-emissive materials that could be used for the purposes taught by Frey et al.

Further with respect to the substituted phenyl groups required by claim 7, Frey et al. teach that aryl groups may be substituted by alkyl groups that are straight or branched-chain and have from 1 to 20 carbon atoms (e.g. see the last two lines on page 12 and p. 13, l. 7-11, of the

Frey et al. reference), and Hu et al. disclose examples of compounds having 4-t-butyl phenyl groups as part of a substituent on a fluorene ring of the indenofluorene structure. Absent a showing of superior/unexpected results commensurate in scope with the claims, it is the examiner's position that it would have been within the level of ordinary skill of a worker in the art at the time of the invention to determine suitable substituents for indenofluorene units within the scope of Frey's formula (IX) structure with knowledge in the art that various substituted aryl groups, and various aryl-substituted groups, were known to be useful as substituents for light-emitting indenofluorene compounds.

9. When making the rejection under 35 U.S.C. 103(a) that is set forth in this Office action, the examiner has taken into consideration the data previously submitted in the Rule 132 Declaration filed August 01, 2008. It is the examiner's position that the data do not demonstrate unexpected results. Even if the examiner were to be persuaded that the data demonstrate unexpected results, the polymers described in the declaration are not commensurate in scope with the claimed polymers. For example, the claim 1 language requiring that at least one of R₁-R₄ "comprises an aryl or heteroaryl group" does not limit the at least one of R₁-R₄ to an aryl or heteroaryl group; the proviso could be met by an aryloxy or heteroaryloxy group, or by an alkyl group that is further substituted by an aryl or heteroaryl group.

10. Any inquiry concerning this communication should be directed to Marie R. Yamnitzky at telephone number (571) 272-1531. The examiner works a flexible schedule but can generally be reached at this number from 7:00 a.m. to 3:30 p.m. Monday and Wednesday-Friday.

Application/Control Number: 10/533,920

Page 8

Art Unit: 1794

The current fax number for all official faxes is (571) 273-8300. (Unofficial faxes to be sent directly to examiner Yamnitzky can be sent to (571) 273-1531.)

/Marie R. Yamnitzky/
Primary Examiner, Art Unit 1794

MRY
May 11, 2009

Notice of References Cited	Application/Control No. 10/533,920	Applicant(s)/Patent Under Reexamination TOWNS ET AL.	
	Examiner Marie R. Yamnitzky	Art Unit 1794	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-6,479,172 B2	11-2002	Hu et al.	428/690
	B	US-			
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N	WO 02/095841 A2	11-2002	WO	Frey et al.	—
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	Peng et al., "Novel polymers for light emitting diodes", Acta Polymerica, Vol. 49, pp. 244-247 (1998).
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



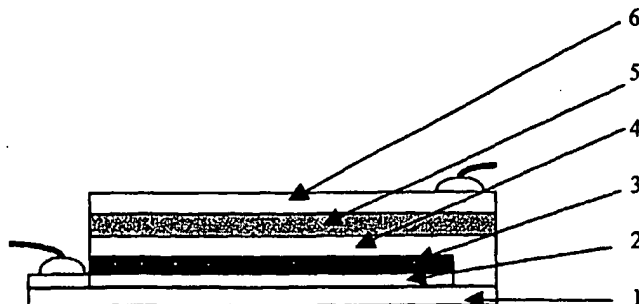
(43) International Publication Date
28 November 2002 (28.11.2002)

PCT

(10) International Publication Number
WO 02/095841 A2

- (51) International Patent Classification⁷: **H01L 51/20**
- (21) International Application Number: **PCT/GB02/02306**
- (22) International Filing Date: **16 May 2002 (16.05.2002)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
0112138.3 18 May 2001 (18.05.2001) GB
0123287.5 27 September 2001 (27.09.2001) GB
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
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— *without international search report and to be republished upon receipt of that report*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: **ELECTROLUMINESCENT DEVICE**



(57) Abstract: An electroluminescent device comprises a hole injecting electrode (2), an electron injecting electrode (5, 6) and at least one organic light emitting layer (4) disposed between said hole injecting electrode (2) and said electron injecting electrode (5, 6) wherein a layered metal chalcogenide layer (3) is disposed between said hole injecting electrode and said light emitting layer.

WO 02/095841 A2

Electroluminescent Device

The present invention relates to novel organic electroluminescent devices which have a novel hole transport layer between the hole generating electrode and the organic light emitting layer. These devices are highly efficient and are easy and cheap to manufacture.

In recent years, there has been considerable interest in light emitting organic materials such as conjugated polymers. Light emitting polymers possess a delocalised pi-electron system along the polymer backbone. The delocalised pi-electron system confers semiconducting properties to the polymer and gives it the ability to support positive and negative charge carriers with high mobilities along the polymer chain. Thin films of these conjugated polymers can be used in the preparation of optical devices such as light-emitting devices. These devices have numerous advantages over devices prepared using conventional semiconducting materials, including the possibility of wide area displays, low dc working voltages and simplicity of manufacture. Devices of this type are described in, for example, WO-A-90/13148, US 5,512,654 and WO-A-95/06400.

The world market for displays based on organic and polymeric light-emitting materials has recently been estimated by Stanford Resources, Inc., to be \$ 200 million in the year 2002 with a strong growth rate which fuels the high industrial interest in this area (D.E. Mentley, "Flat Information Displays: Market and Technology Trends", 9th edition, 1998). Efficient and highly stable LED devices with low power consumption, which fulfill commercial requirements, have been prepared by a number of companies and academic research groups (see, for example, R.H. Friend et al., *Nature* 1999, 397, 12).

At the moment, great efforts are dedicated to the realization of a full-colour, all plastic screen. The major challenges to achieve this goal are: (1) access to conjugated polymers emitting light of the three basic colours red, green and blue; and (2) the conjugated polymers must be easy to process and fabricate into full-colour display

structures. Organic electroluminescent devices such as polymeric LEDs (PLEDs) show great promise in meeting the first requirement, since manipulation of the emission colour can be achieved by changing the chemical structure of the organic emissive compound. However, while modulation of the chemical nature of the emissive layer is often easy and inexpensive on the lab scale it can be an expensive and complicated process on the industrial scale. The second requirement of the easy processability and build-up of full-colour matrix devices raises the question of how to micro-pattern fine multicolour pixels and how to achieve full-colour emission. Inkjet printing and hybrid inkjet printing technology have recently attracted much interest for the patterning of PLED devices (see, for example, R.F. Service, *Science* 1998, 279, 1135; Wudl et al., *Appl. Phys. Lett.* 1998, 73, 2561; J. Bharathan, Y. Yang, *Appl. Phys. Lett.* 1998, 72, 2660; and T.R. Hebner, C.C. Wu, D. Marcy, M.L. Lu, J. Sturm, *Appl. Phys. Lett.* 1998, 72, 519).

At their most basic, organic electroluminescent devices generally comprise an organic light emitting material which is positioned between a hole injecting electrode and an electron injecting electrode. The hole injecting electrode (anode) is typically a transparent tin-doped indium oxide (ITO)-coated glass substrate. The material commonly used for the electron injecting electrode (cathode) is a low work functions metal such as calcium or aluminium.

The materials that are commonly used for the organic light emitting layer include conjugated polymers such as poly-phenylene-vinylene (PPV) and derivatives thereof (see, for example, WO-A-90/13148), polyfluorene derivatives (see, for example, A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, and E. P. Woo, *Appl. Phys. Lett.* 1998, 73, 629, WO-A-00/55927 and Bernius et al., *Adv. Materials*, 2000, 12, No. 23, 1737), polynaphthylene derivatives and polyphenanthrenyl derivatives; and small organic molecules such as aluminium quinolinol complexes (Alq₃ complexes: see, for example US-A-4,539,507) and quinacridone, rubrene and styryl dyes (see, for example, JP-A-264692/1988). The organic light emitting layer can comprise mixtures or discrete layers of two or more different emissive organic materials.

Typical device architecture is disclosed in, for example, WO-A-90/13148; US-A-5,512,654; WO-A-95/06400; R.F. Service, *Science* 1998, 279, 1135; Wudl et al., *Appl. Phys. Lett.* 1998, 73, 2561; J. Bharathan, Y. Yang, *Appl. Phys. Lett.* 1998, 72, 2660; T.R. Hebner, C.C. Wu, D. Marcy, M.L. Lu, J. Sturm, *Appl. Phys. Lett.* 1998, 72, 519; and WO 99/48160; the contents of which references are incorporated herein by reference thereto.

The injection of holes from the hole injecting layer such as ITO into the organic emissive layer is controlled by the energy difference between the hole injecting layer work function and the highest occupied molecular orbital (HOMO) of the emissive material, and the chemical interaction at the interface between the hole injecting layer and the emissive layer. The deposition of high work function organic materials on the hole injecting layer, such as poly(styrene sulfonate)-doped poly (3,4-ethylene dioxythiophene) (PEDOT/PSS), N,N'-diphenyl-N,N'-(2-naphthyl)-(1,1'-phenyl)-4,4'-diamine (NBP) and N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), provides "hole transport" layers which facilitate the hole injection into the light emitting layer, transport holes stably from the hole injecting electrode and obstruct electrons. These layers are effective in increasing the number of holes introduced into the light emitting layer. However, the surface of ITO is not well defined and the chemistry at the interface with these conventional hole transport materials is hard to control.

As an alternative to the high work function organic materials such as PEDOT/PSS, high resistivity inorganic layers have been proposed for use as hole transport layers in, for example, EP-A-1009045, EP-A-1022789, EP-A-1030539 and EP-A-1041654. EP-A-1022789 discloses an inorganic hole transport layer which is capable of blocking electrons and has conduction paths for holes. The layer has a high resistivity, stated to be preferably in the region of 10^3 to $10^8 \Omega\text{-cm}$. The materials which are disclosed have the general formula $(\text{Si}_{1-x}\text{Ge}_x)\text{O}_y$ wherein $0 \leq x \leq 1$ and $1.7 \leq y \leq 2.2$. The work function of this hole transport layer is not well defined and is likely to vary depending upon the actual identity of x and y. EP-A-1083776 and EP-A-1111967 disclose EL devices having an inorganic hole transport layer that comprises a

combination of a metal chalcogenide and an inorganic compound of an element of Group 5A to Group 8 of the periodic table. It is essential that both components are present to provide the desired effect of tuning the work function and there is no suggestion that the metal chalcogenides should be layered metal chalcogenides. US-A-6023128 discloses an EL device having a hole transport layer comprising a matrix in which are embedded transition metal chalcogenide clusters which are stabilised by organic ligand shells. Tuning of the electronic properties is achieved through the quantum size effect exerted by these clusters. There is no disclosure of the use of single continuous layers of a layered metal chalcogenide as a hole transport layer.

There is still a need, however, for a hole transport material which is superior to these prior art materials, especially one which is chemically inert at the interface with the organic light emitting layer and which has properties which would enable the simple, low cost manufacture of devices which have excellent power efficiency, a low drive voltage and a high level of luminance.

It is therefore an object of the present invention to provide an electroluminescent device which incorporates a novel inorganic hole transport layer, said electroluminescent device having superior properties both in its ease of manufacture and in its performance.

Thus, in a first aspect of the present invention there is provided an electroluminescent device comprising a hole injecting electrode, an electron injecting electrode and at least one organic light emitting layer disposed between said hole injecting electrode and said electron injecting electrode, wherein a layered metal chalcogenide layer is disposed between said hole injecting electrode and said light emitting layer, the chalcogen component of said chalcogenide being chosen from sulfur, selenium and tellurium.

The layered metal chalcogenides are a well-known class of compounds (e.g. see Physics and Chemistry of Materials With Layered Structures, pub. D. Reidel/Dordrecht-Holland/Boston-USA) and include any compounds comprising metal atoms and

chalcogen atoms chosen from sulfur, selenium and tellurium in a layer-type structure. Examples include layered metal dichalcogenides and layered metal monochalcogenides. The layered metal dichalcogenides have the chemical formula MX_2 wherein M represents a metal and X represents sulfur, selenium or tellurium. The structure of the layered metal dichalcogenides preferably includes one sheet of metal atoms sandwiched between two sheets of chalcogen atoms. In the layered metal dichalcogenides, the metallic component M is preferably selected from transition metals such as titanium, zirconium, hafnium, vanadium, tantalum, niobium, molybdenum and tungsten and non-transition metals such as tin. More preferred are niobium, molybdenum, tantalum, tin and tungsten, and most preferred are niobium, molybdenum and tantalum. More preferred chalcogens are sulfur and selenium. Metals that form monochalcogenides include gallium, indium and thallium.

As we explain in greater detail below, the layered metal chalcogenides have several properties which make them particularly suitable for use as hole transport layers. They are chemically inert, having no dangling bonds, thus overcoming the problems of chemical interactions experienced at the interfaces of the prior art hole transporting layers referred to above with the organic light emitting layer and the anode. The layered metal chalcogenides have a high work function which enables easier transfer of the holes from the metal chalcogenide layer to the organic light emitting layer. Furthermore, they can be processed simply and cheaply using chemical processes to give thin films.

The structure of the metal chalcogenides comprises sheets of metal atoms sandwiched between sheets of chalcogen atoms. In the layered metal dichalcogenides, for example, the metallic sheet is covalently bonded to the two adjacent sheets of chalcogens. Two adjacent MX_2 layers are kept together by van der Waals forces. This structure leads to extremely anisotropic mechanical, chemical and electrical properties. Exposed surfaces of these materials have no dangling bonds and, hence, are chemically inert. This makes them particularly suitable for use as hole transport layers in electroluminescent devices as it removes the problem of chemical reactions at the

interfaces with the hole injecting layer (e.g. ITO) and the organic light emitting layer (e.g. PPV) which reduce the efficiency and effective lifetime of the prior art devices.

The layered metal chalcogenides exhibit high work functions in the range 4-6.5 eV, and 5-6.5 eV is particularly preferred. For example, the work functions of niobium diselenide, molybdenum disulfide, tin disulfide, tantalum disulfide, vanadium diselenide, indium selenide and gallium selenide are 5.9, 4.8, 5.2, 5.2, 5.6, 4.55 and 5.8 eV, respectively [measured by a photoemission technique as disclosed in T. Shimada, F. S. Ohuchi and B. A. Parkinson, *Jap. J. App. Phys.* 33, 2696 (1994)]. The high work function of these materials makes them particularly suitable for use as hole transport layers, as these work functions are close in value to the ionization potentials of the organic light emitting layers, facilitating easy hole transfer to said emissive layer. The high work function, reasonable conductivity and the inertness of exposed surfaces of the layered metal chalcogenides greatly facilitate hole injection from the hole injecting electrode (e.g. ITO) into the emissive layer in the electroluminescent device of the present invention, making the devices particularly efficient.

The electronic properties of the layered metal chalcogenides vary widely, from insulators through semiconductors and semi-metals to true metals. The resistivity of the layered metal chalcogenides ranges from very low values such as approximately 4×10^{-4} Ω -cm for niobium diselenide and tantalum disulfide to values such as 10 Ω -cm in molybdenum disulfide. As already noted above, prior disclosures of inorganic hole transport layers, such as those in EP-A-1022789, teach preferred resistivities of 1×10^3 - 1×10^8 Ω -cm. The low resistivity exhibited by some of the layered metal chalcogenides may result in a reduction in the required drive voltage for some of the devices of the present invention.

The structure of the layered metal dichalcogenides includes one hexagonal packed sheet of metal atoms sandwiched between two hexagonal sheets of chalcogen atoms. The coordination of the metal atoms by the chalcogen atoms is either hexagonal (e.g. titanium disulfide and vanadium disulfide) or trigonal prismatic (e.g. molybdenum disulfide and

niobium disulfide). The MX_2 layers are kept together by van der Waals forces and several stacking polytypes exist (see Figure 1). The weak bonding between layers, where a layer consists of a monolayer of metal atoms clad together by covalently-bonded chalcogens, leads to extremely anisotropic mechanical and electrical properties. For example, the conductivity perpendicular to the planes is down by a factor of at least 10^2 on that in the planes for molybdenum disulfide [see J.A.Wilson and A. D. Yoffe, *Adv. Phys.* 18, 193 (1969)].

The structure of the layered metal monochalcogenides includes two hexagonal packed sheets of metal atoms sandwiched between two hexagonal sheets of chalcogen atoms in the sequence X-M-M-X. In the binary compounds, the cations prefer the tetrahedral coordination. The bonding in the X-M-M-X layer is covalent. The metal-metal bonds are responsible for the semiconducting behavior of these materials. The layers are kept together by van der Waals forces and several stacking polytypes exist. The weak bonding between layers leads to extremely anisotropic mechanical and electrical properties.

The coordination and the oxidation state of the metal atom determine the electronic properties of the material. For example, the group V metal atoms (niobium and tantalum) are in a trigonal prismatic coordination and the corresponding dichalcogenide materials are metals, while group VI atoms (molybdenum and tungsten) are also in a trigonal prismatic coordination but have a full d_z band and hence are semiconductors. Molybdenum disulfide has both a hexagonal and a trigonal prismatic coordination, and can thus be either metallic or semiconducting respectively.

The absorption spectra of the metallic metal chalcogenides shows that the materials absorb throughout the IR and visible region. However, for thin films of trigonal prismatic materials such as niobium diselenide, the free carrier absorption is below 1 eV and is well separated from the direct absorption edge above 2 eV [see J.A.Wilson and A. D. Yoffe, *Adv. Phys.* 18, 193 (1969)]. Therefore, by processing very thin films of the layered metal chalcogenides, their absorption of the emission is minimized. Thus,

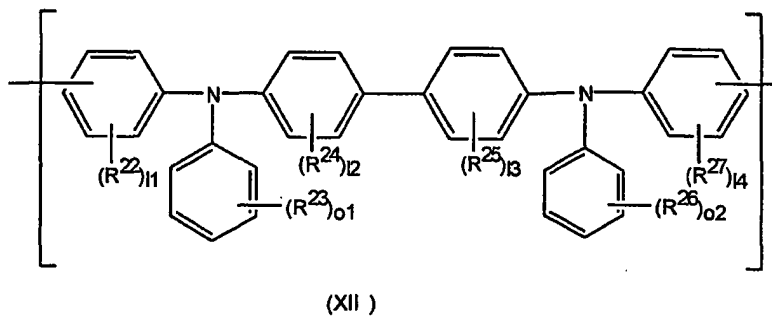
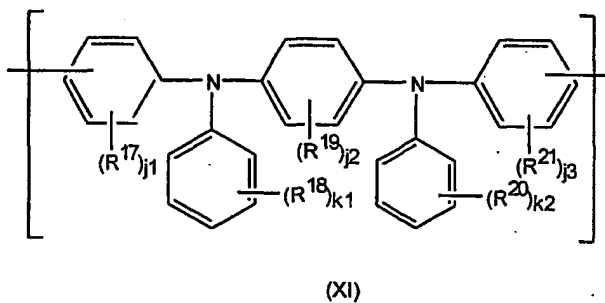
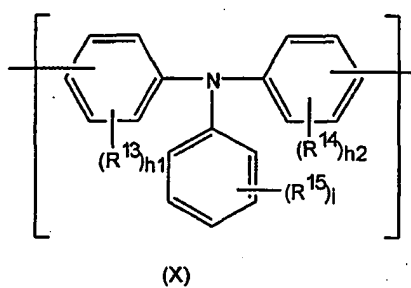
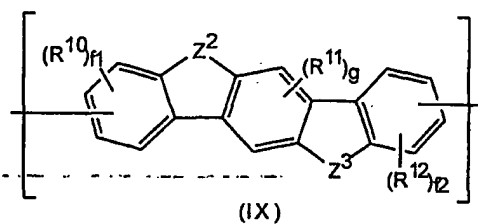
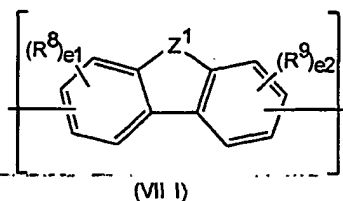
although the thickness of the layer is not critical, the layered metal chalcogenide hole transport layer preferably has a thickness of from 3 to 20 nm, more preferably from 3 to 10 nm, and most preferably from 3 to 7 nm. Thicker films, although still effective, can absorb greater than 20% of the emitted light and thus decrease the light emission.

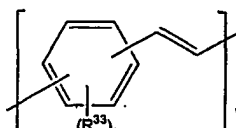
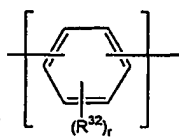
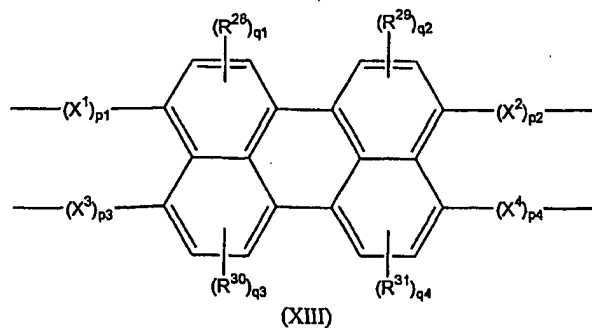
Preferably, the layered metal chalcogenide is the only hole transporting material. Furthermore, it should be understood that the layered metal chalcogenide hole transport layer forms a single continuous thin sheet on the hole injecting electrode, c.f. the clusters suspended in a matrix disclosed in US-A-6023128.

Particularly good properties can be obtained in some cases if the layered metal chalcogenide hole transport layer is annealed at a temperature of at least 100°C (e.g. 250°C) before the emissive layer is deposited on it, as it improves the order in the film of some of the layered metal chalcogenide materials and enhances their conductivity.

The light emitting layer can comprise one or more organic light emitting materials. Where there is more than one organic light emitting material, these can be disposed as separate, discrete layers or as mixtures of said materials in a single layer. Any organic light emitting materials can be used for the light emitting layer. Suitable examples include: conjugated polymers such as poly-phenylene-vinylene (PPV) and derivatives thereof (see, for example, WO-A-90/13148), polyfluorene derivatives (see, for example, A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, and E. P. Woo, *Appl. Phys. Lett.* 1998, 73, 629, WO-A-00/55927 and Bernius et al., *Adv. Materials*, 2000, 12, No. 23, 1737), polynaphthylene derivatives, polyindenofluorene derivatives and polyphenanthrenyl derivatives; and small organic molecules such as aluminium quinolinol complexes (Alq3 complexes: see, for example US-A-4,539,507), complexes of transition metals, lanthanides and actinides with organic ligands such as TMHD (see WO-A-00/26323) and quinacridone, rubrene and styryl dyes (see, for example, JP-A-264692/1988); the contents of which references are incorporated herein by reference thereto.

Specific examples of preferred light emitting polymeric materials include polymers which include the following conjugated units of formulae (VIII), (IX), (X), (XI), (XII), (XIII), (XIV) and (XV). These polymers can be homopolymers or can contain two or more different conjugated units, e.g. alternating AB copolymers and terpolymers, and statistical copolymers and terpolymers.





wherein:

each of R^8 to R^{15} and R^{17} to R^{33} is the same or different and is selected from the group consisting of alkyl groups as defined below, haloalkyl groups as defined below, alkoxy groups as defined below, alkoxyalkyl groups as defined below, aryl groups as defined below, aryloxy groups as defined below, aralkyl groups as defined below and groups of formula $-COR^{16}$ wherein R^{16} is selected from the group consisting of hydroxy groups, alkyl groups as defined below, haloalkyl groups as defined below, alkoxy groups as defined below, alkoxyalkyl groups as defined below, aryl groups as defined below, aryloxy groups as defined below, aralkyl groups as defined below, amino groups, alkylamino groups the alkyl moiety of which is as defined below, dialkylamino groups wherein each alkyl moiety is the same or different and is as defined below, aralkyloxy groups the aralkyl moiety of which is as defined below and haloalkoxy groups comprising an alkoxy group as defined below which is substituted with at least one halogen atom,

or, where r or s is an integer of 2, the 2 groups R^{32} or R^{33} respectively may, together with the ring carbon atoms to which they are attached, form a heterocyclic group having from 5 to 7 ring atoms, one or more of said ring atoms being a heteroatom selected from the group consisting of nitrogen, oxygen and sulfur atoms;

each of Z^1 , Z^2 and Z^3 is the same or different and is selected from the group consisting of O, S, SO, SO₂, NR³, N⁺(R^{3'})(R^{3''}), C(R⁴)(R⁵), Si(R^{4'})(R^{5'}) and P(O)(OR⁶), wherein R³, R^{3'} and R^{3''} are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups as defined below, haloalkyl groups as defined below, alkoxy groups as defined below, alkoxyalkyl groups as defined below, aryl groups as defined below, aryloxy groups as defined below, aralkyl groups as defined below, and alkyl groups as defined below which are substituted with at least one group of formula -N⁺(R⁷)₃ wherein each group R⁷ is the same or different and is selected from the group consisting of hydrogen atoms, alkyl groups as defined below and aryl groups as defined below, R⁴, R⁵, R^{4'} and R^{5'} are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups as defined below, haloalkyl groups as defined below, alkoxy groups as defined below, halogen atoms, nitro groups, cyano groups, alkoxyalkyl groups as defined below, aryl groups as defined below, aryloxy groups as defined below and aralkyl groups as defined below or R⁴ and R⁵ together with the carbon atom to which they are attached represent a carbonyl group, and R⁶ is selected from the group consisting of hydrogen atoms, alkyl groups as defined below, haloalkyl groups as defined below, alkoxyalkyl groups as defined below, aryl groups as defined below, aryloxy groups as defined below and aralkyl groups as defined below;

each of X¹, X², X³ and X⁴ is the same or different and is selected from:

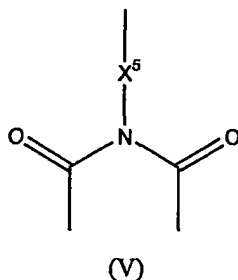
arylene groups which are aromatic hydrocarbon groups having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted by at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined below, haloalkyl groups as defined below, alkoxyalkyl groups as defined below, aryloxy groups as defined below and alkoxy groups as defined below;

straight or branched-chain alkylene groups having from 1 to 6 carbon atoms;

straight or branched-chain alkenylene groups having from 2 to 6 carbon atoms;

and

straight or branched-chain alkynylene groups having from 1 to 6 carbon atoms; or X^1 and X^2 together and/or X^3 and X^4 together can represent a linking group of formula (V) below:



wherein X^5 represents an arylene group which is an aromatic hydrocarbon group having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted by at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined below, haloalkyl groups as defined below, alkoxyalkyl groups as defined below, aryloxy groups as defined below and alkoxy groups as defined below;

each of e1, e2, f1 and f2 is the same or different and is 0 or an integer of 1 to 3;

each of g, q1, q2, q3 and q4 is the same or different and is 0, 1 or 2;

each of h1, h2, j1, j2, j3, l1, l2, l3, l4, r and s is the same or different and is 0 or an integer of 1 to 4;

each of i, k1, k2, o1 and o2 is the same or different and is 0 or an integer of 1 to 5; and

each of p1, p2, p3 and p4 is 0 or 1;

the alkyl groups above are straight or branched-chain alkyl groups having from 1 to 20 carbon atoms;

the haloalkyl groups above are alkyl groups as defined above which are substituted with at least one halogen atom;

the alkoxy groups above are straight or branched-chain alkoxy groups having from 1 to 20 carbon atoms;

the alkoxyalkyl groups above are alkyl groups as defined above which are substituted with at least one alkoxy group as defined above; and

the aryl group above and the aryl moiety of the aralkyl groups (which have from 1 to 20 carbon atoms in the alkyl moiety) and the aryloxy groups above is an aromatic hydrocarbon group having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted with at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above and alkoxy groups as defined above.

The particularly preferred light emitting polymers include homopolymers, copolymers and terpolymers which comprise groups of formulae (VIII), (IX), (X), (XIV) and (XV), examples of which include PPV, poly(2-methoxy-5-(2'-ethyl)hexyloxyphenylene-vinylene) ("MEH-PPV"), PPV derivatives such as dialkoxy and dialkyl derivatives, polyfluorene derivatives and related copolymers; and the most preferred polymers include PPV, MEH-PPV, poly (2,7-(9,9-di-*n*-hexylfluorene)), poly (2,7-(9,9-di-*n*-octylfluorene)), poly (2,7-(9,9-di-*n*-octylfluorene)-(1,4-phenylene-((4-*sec*-butylphenyl)imino)-1,4-phenylene)) ("TFB"), and poly (2,7-(9,9-di-*n*-octylfluorene)-3,6-benzothiadiazole) ("F8BT"). The most preferred light emitting organic molecules include Alq3 complexes.

The thickness of the light emitting layer or layers is not critical. The precise thickness of the layer or layers will vary depending upon factors such as the identity of the material or materials of the light emitting layer or layers and the identity of the other components of the device. However, typically the thickness of the light emitting layer (or combined thickness if there is more than one layer) is from 1 to 250 nm, preferably from

50 to 120 nm, yet more preferably from 70 to 100 nm, and most preferably from 75 to 85 nm.

The organic light emitting layer can be deposited on the layered metal chalcogenide hole transport layer using any method suitable for the deposition of such organic layers. As the layered metal chalcogenides are not soluble in organic solvents, spin coating from solution of the organic light emitting material is particularly suitable for this purpose (see, for example, WO-A-90/13148).

The electroluminescent device of the present invention may typically have the stacked configuration of substrate (e.g. glass), a hole injecting electrode (e.g. ITO), a layered metal chalcogenide hole transport layer, an organic light emitting layer (e.g. a polyfluorene), and an electron injecting electrode (e.g. Ca/Al). Alternatively, the device may have the inversely stacked configuration of substrate, an electron injecting electrode, an organic light emitting layer, a layered metal chalcogenide hole transport layer, and a hole injecting electrode.

Any suitable technique known in the art may be employed to deposit the layered metal chalcogenide hole transport layer on the anode. However, the chemical route is preferred since ultra thin films can be deposited on the anode in a low cost process.

A suitable chemical process for depositing the layered metal dichalcogenides on the anode is based on one developed by Frindt et al. [see P. Joensen, R. F. Frindt and S. R. Morrison, *Mat. Res. Bull.* 21, 457 (1986) and US Patent 4,996,108]. This process involves the following steps:

- (a) intercalation of lithium atoms into the MX_2 compounds;
- (b) addition of water to the intercalated material, resulting in the reduction of the water by the lithium atoms. The resulting hydrogen gas which is evolved between the MX_2 layers breaks up the stacking of the layers (exfoliation) and single layers of MX_2 which are suspended in the water are produced as a result;

- (c) addition of a water immiscible solvent to the single layer water suspension of MX_2 , followed by agitation of the resulting mixture, producing a thin film of MX_2 which is formed at the solvent/water interface; and
- (d) dipping the lower end of a wet ITO-coated glass substrate into the solvent/water interface, resulting in the spread of the MX_2 film as a thin oriented film on the ITO surface. The MX_2 films are oriented with the c-axis perpendicular to the ITO-coated substrate.

The layered metal chalcogenide hole transport layer provides excellent conduction paths for holes generated by the hole injecting electrode. Some of the layered metal chalcogenides which are semiconducting materials may also be capable to some extent of blocking electrons from escaping from the light emitting organic layer, thus helping to balance the electron and hole currents in the light emitting layer and to enhance their capture. However, the ability to block electrons can be greatly enhanced by depositing a layer of a material, capable of restraining migration of electrons from the emissive layer, between the inorganic layered metal chalcogenide hole transport layer and the light emitting organic layer.

Thus, in a particularly preferred embodiment of the device of the invention, there is provided a layer of a material between the organic light emitting layer and layered metal chalcogenide hole transport layer which is capable of restraining migration of electrons from said organic light emitting layer to said layered metal chalcogenide hole transport layer. This material can, for example, be one of the materials known from the prior art to be capable of restraining migration of electrons from the organic light emitting layer, e.g. the oxides, carbides, nitrides, silicides and borides of metals and metalloids which are disclosed in EP-A-1022789 and EP-A-1041654, such as those of general formula $(\text{Si}_{1-x}\text{Ge}_x)\text{O}_y$ wherein $0 \leq x \leq 1$ and $1.7 \leq y \leq 2.2$.

It is particularly preferable, however, for the thin layer of material that is capable of restraining migration of electrons to be an oxide of the same metal as that of said metal chalcogenide layer. These metal oxides act as highly effective electron blockers.

Furthermore, the deposition of the metal oxide layer is very simple as it can be effected by oxidising the exposed surface of the layered metal chalcogenide layer after its deposition on the hole injecting layer. The metal oxide can be stoichiometric or non-stoichiometric; the actual composition of the oxide layer may vary depending upon the oxidation conditions used to produce said layer. Additionally, the polymer solutions wet the metal oxide layers much better than the layered metal chalcogenide layers, resulting in fewer pin holes and lower leakage currents (i.e. higher efficiencies).

These preferred organic electroluminescent devices which incorporate the metal oxides (MOs) on the layered metal chalcogenide (LMC) layer have the following typical structure: glass/ITO/LMC/MO/organic light emitting layer/Ca/Al. Such devices have a low manufacturing cost, a low operating voltage and are highly efficient.

Methods for the deposition of the electron blocking metal oxide film include various physical and chemical film forming methods such as sputtering and evaporating. Oxidation of the layered metal chalcogenide layer in an oxygen plasma generator is particularly preferable. Typical oxidation is carried out in an RF oxygen plasma generator at 0.3-0.5 mbar oxygen pressure and 250 W. The length of treatment in the plasma generator controls the thickness of the oxide film. The preferred thickness of the metal oxide film will vary depending upon the nature of the device and it is not critical to the efficiency of the device. However, particularly efficient electron-hole balancing is achieved in devices comprising a 1-10 nm metal oxide film; metal oxide films having a thickness of 2 to 6 nm are more preferred; and metal oxide films having a thickness of 2-3 nm are most preferred. Films having a thickness of less than 1 nm can have reduced effectiveness in electron blocking while hole injection into the organic light emitting layer can be less efficient in some instances in films having a thickness of greater than 4 nm. The oxidation rate depends on the LMC/MO material involved and the generator set-up.

In devices which include an electron blocking thin film such as an oxide of the metal of the layered metal chalcogenide layer, the organic light emitting layer is

deposited on the electron blocking film layer. Since the layered metal chalcogenide and metal oxide layers are non-soluble in organic solvents, the organic emitting layer can be deposited by spin coating from solution onto the inorganic layer, which is a simple and low-cost procedure.

In some devices, an "electron transport" layer is also provided between the electron injecting layer and the light emitting layer (e.g. suitable compounds include oxides of alkali metals, alkaline earth metals or lanthanoid elements having a work function of up to 4 eV, such as those disclosed in EP-A-1009045). These facilitate the electron injection into the light emitting layer, they transport electrons stably from the electron injecting layer and they obstruct holes. These layers are effective for increasing the number of electrons into the light emitting layer. Particularly preferred are strontium oxide, magnesium oxide, calcium oxide, lithium oxide, rubidium oxide, potassium oxide, sodium oxide and cesium oxide. The thickness of the electron transport layer will vary depending upon the material of which it is comprised, but it is typically from 0.1 to 2 nm and preferably from 0.3 to 0.8 nm.

The substrate on which the organic electroluminescent device of the present invention can be formed is any which is typically used in such devices, examples of which include glass, quartz and crystalline substrates of Si, GaAs, ZnSe, ZnS, GaP and InP. Of these, glass substrates are particularly preferred.

The hole injecting electrode can be formed from any material typically used for this purpose in electroluminescent devices. Examples of suitable materials include tin-doped indium oxide (ITO), zinc-doped indium oxide (IZO), indium oxide, tin oxide and zinc oxide, of which ITO is particularly preferred. The thickness of the hole injecting electrode will vary depending upon the identity of the hole injecting material and of the other components of the electroluminescent device. Typically, the electrode has a thickness of from 50 to 500 nm, particularly from 50 to 300 nm.

The electron injecting electrode can be formed from any material typically used for this purpose in electroluminescent devices. Examples of suitable materials include low work function metals such as potassium, lithium, sodium, magnesium, lanthanum, cerium, calcium, strontium, barium, aluminium, silver, indium, tin, zinc and zirconium, and binary or ternary alloys containing such metals. Of these, successive layers of aluminium and calcium and aluminium-calcium alloys containing from 1 to 20% by weight of calcium are preferred. The thickness of the electron injecting electrode will vary depending upon the identity of the electron injecting material and of the other components of the electroluminescent device. Typically, the electrode has a thickness of from 0.1 to 500 nm, preferably at least 1 nm.

The typical organic electroluminescent devices of the present invention include an an inorganic layered metal chalcogenide hole transport layer, an inorganic metal-oxide electron blocking layer, and an organic light emitting layer sandwiched between the anode and cathode. These devices are cheap to manufacture because the processes needed to deposit the layers are simple and most of the layered metal chalcogenides are inexpensive and readily available. In particular, the all-chemical inexpensive device processing techniques outlined above offer an easy-to-prepare, low-cost device. The electroluminescent devices of the present invention are highly efficient, with a power efficiency of greater than 10 Lum/Watt in some devices, and remarkably bright, with a luminance at 6V of greater than 60,000 Cd/m² in some devices. The hybrid organic/inorganic device has both the advantages of the organic materials and the inorganic materials, and the outstanding performance of the devices of the present invention demonstrates organic/inorganic synergism.

The present invention may be further understood by consideration of the following examples, with reference to the following drawings in which:

Figure 1 shows the atomic structure of 2H-MoS₂;

Figure 2 shows a schematic representation of an electroluminescent device according to the present invention having a layered metal dichalcogenide hole transport layer;

Figures 3 to 5 show I-V-L spectra of glass/ITO/MS₂/F8BT:TFB/Ca/Al devices according to the present invention;

Figure 6 shows a schematic representation of an electroluminescent device according to the present invention having a layered metal dichalcogenide hole transport layer and a metal oxide electron blocking layer;

Figure 7 shows I-V-L spectra of glass/ITO/NbSe₂/Nb₂O₅/F8BT:TFB/Ca/Al devices according to the present invention;

Figure 8 shows power and light efficiency spectra of glass/ITO/NbSe₂/Nb₂O₅/F8BT:TFB/Ca/Al devices according to the present invention;

Figure 9 shows I-V-L spectra of glass/ITO/MoS₂/MoO₃/F8BT:TFB/Ca/Al devices according to the present invention;

Figure 10 shows power and light efficiency spectra of glass/ITO/MoS₂/MoO₃/F8BT:TFB/Ca/Al devices according to the present invention;

Figure 11 shows I-V-L spectra of glass/ITO/TaS₂/Ta₂O₅/F8BT:TFB/Ca/Al devices according to the present invention;

Figure 12 shows power and light efficiency spectra of glass/ITO/TaS₂/Ta₂O₅/F8BT:TFB/Ca/Al devices according to the present invention;

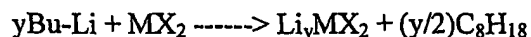
We shall first describe a process for the production of the substrate/hole injecting layer/layered metal chalcogenide hole transport layer structure, and then describe the production of two alternative types of organic electroluminescent devices based on this structure, one with and one without a metal oxide layer between the layered metal chalcogenide layer and the organic light emitting layer. In these examples, the layered metal chalcogenides employed are all layered metal dichalcogenides.

Li Intercalation, exfoliation and film formation:

Intercalation

n-Butyllithium (Bu-Li) in hexane solution was used for the intercalation of lithium atoms into the layered metal dichalcogenide compounds. In a typical reaction,

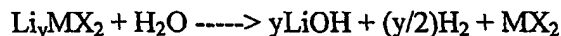
0.5 g of commercial layered metal dichalcogenide (MX_2) powder was soaked in 1.6M Bu-Li in hexane under argon in dried Schlenkware for 3 days in a procedure based on that disclosed in D. W. Murphy, F. J. Di Salvo, G. W. Hull Jr. and J. V. Waszczak, *Inorg. Chem.* 15, 17 (1976). The intercalation reaction is as follows:



The product, Li_yMX_2 , was washed in anhydrous hexane, dried under vacuum, then transferred and stored in a glove box. In the intercalated compounds, the lithium atoms are situated in the van der Waals gap between the MX_2 layer [see R. H. Friend and A. D. Yoffe, *Adv. Phys.* 36, 1 (1987)].

Exfoliation

The process used is based on that described in P. Joensen, R. F. Frindt and S. R. Morrison, *Mat. Res. Bull.* 21, 457 (1986) and US Patent 4,996,108. A vial was loaded in the glove box with 15-20 mg of the Li_yMX_2 produced in the intercalation step above and then taken out. Immediately, 5-10 ml of deionised water were added and the solution was sonicated (typically for 1 hour). An exfoliation reaction takes place as follows:



The hydrogen gas evolved in between the MX_2 layers breaks up the stacking of the layers producing single layers of MX_2 (SL) which are suspended in the water. The SL suspension was centrifuged and the sediment was washed/agitated and centrifuged again until the pH of the supernatant was lowered to 7 indicating there was no lithium hydroxide left in the sediment.

Film forming:

The process used is based on that described in P. Joensen, R. F. Frindt and S. R. Morrison, *Mat. Res. Bull.* 21, 457 (1986) and US Patent 4,996,108. 3 ml of deionised water were added to the SL sediment and the suspension sonicated for several minutes. 2-

3 ml of xylene or toluene were then added to the sonicated SL suspension. The solvents do not mix and the inorganic material is in the water (lower) phase. Once the vial was shaken, a thin MX_2 film grew on the interface between the water and the organic solvent and also climbed up the walls of the vial. It should be noted that in some instances, further sonications may be performed after addition of the solvent and before shaking, depending on the nature of the materials used and the type of film wanted. A wetted, clean and oxygen plasma treated ITO coated glass substrate (prepared as described in, for example, WO-A-90/13148; 1, 2 in Figures 2 and 6) was then dipped into the interface. The MX_2 thin film (3 in Figures 2 and 6) at the interface spread on to the substrate. The thickness of the film was controlled by the concentration of the SL suspension, and was typically 4-7 nm [determined by AFM (atomic force spectroscopy) and XPS (X-ray photoelectron spectroscopy) measurements].

Device structure

The thin film of organic light emitting material can be coated onto the surface of the inorganic layer produced above using any technique suitable for this purpose. Spin coating from solutions of polymer in organic solvents (disclosed, for example, in WO-A-90/13148) is particularly preferred. In the following examples, a polyfluorene blend of poly (2,7-(9,9-di-*n*-octylfluorene)-(1,4-phenylene-((4-*sec*-butylphenyl)imino)-1,4-phenylene)) ("TFB"), and poly (2,7-(9,9-di-*n*-octylfluorene)-3,6-benzothiadiazole) ("F8BT") [F8BT:TFB (3:1)] in xylene at a concentration of 15 mg/ml was spun on the inorganic layer of the coated substrate produced as described above (spinning took place at 2500 rpm for 60 seconds, gradual acceleration being employed to reach the final spinning speed) to yield a film thickness of 75-80 nm (4 in Figures 2 and 6).

To complete the device, the electron injecting layer was then deposited on the upper surface of the organic light emitting film deposited on the hole transport layer as described above. Any material suitable for use as an electron injecting material can be used, and examples of such materials and means for their deposition are given above. In the present examples a layer of calcium (5 in Figures 2 and 6) was first deposited by

evaporation at a pressure of $<8 \times 10^{-6}$ mbar on the surface of the polymer film followed by evaporation thereon of a layer of aluminium (6 in Figures 2 and 6) at a pressure of $<5 \times 10^{-6}$ mbar.

In these examples, two sets of devices were fabricated.

In the first set of devices, molybdenum disulfide, niobium diselenide or tantalum disulfide were deposited on the ITO layer so as to act as the hole transport layer before depositing the polymer layer (i.e. there was no oxide layer between the metal dichalcogenide layer and the polymer layer) as shown in Figure 2 (not to scale). In addition, for each metal dichalcogenide, a device was also produced in which the metal dichalcogenide layer was (at a pressure of 10^{-5} mbar and a temperature of 230-240°C for 10 hours) before deposition of the polymer layer. This was done to study the effect of annealing the metal dichalcogenide films on the device performance.

A control device having the structure: glass/ITO/PEDOT:PSS/F8BT:TFB/Ca/Al was also prepared with each batch of devices in order to compare performances with this prior art device.

The I-V-L spectra are shown in Figures 3 to 5 for 6 devices (3 materials, annealed and unannealed) and the data that can be derived from these are listed in Table 1 below.

Table 1

MX ₂ material	Current density at 6V (mA/cm ²)	Luminance at 6V (cd/m ²)
TaS ₂ unannealed	68	1.4
TaS ₂ annealed	250	7.0
MoS ₂ unannealed	2660	110
MoS ₂ annealed	2140	300
NbSe ₂ unannealed	590	120
NbSe ₂ annealed	2440	490
PEDOT-PSS	1500	60000

Performance for the device structure shown in Figure 2 with MX₂ as hole transport layer

The low current density and luminance values obtained for tantalum disulfide (TaS₂) are probably due to the non-continuity of the film observed by both XPS and AFM measurements. The lower current density observed in the device having an annealed molybdenum disulfide (MoS₂) layer as compared to that in the unannealed film is due to the metal to semiconductor phase transition that the material undergoes upon annealing [see J.A.Wilson and A. D. Yoffe, *Adv. Phys.* 18, 193 (1969)]. Annealing can be seen to result in an improvement in the luminance of the devices in each case.

In the second set of devices, the metal dichalcogenide layer was treated with oxygen plasma at 250W for 1, 5, 10 or 20 minutes. This resulted in the formation of a thin metal oxide film on the surface of the metal dichalcogenide layer (7 in Figure 6). The longer the oxygen plasma treatment, the thicker the metal oxide layer that was produced. As explained above, it was hoped that this would result in an improvement in the electron capturing properties, increasing the electron retention in the light emitting polymer layer and therefore, hopefully, increasing the luminance. In the case of

molybdenum disulfide, the composition of the oxide layer is MoO_3 , while for tantalum disulfide and niobium diselenide, the oxide composition is Ta_2O_5 and Nb_2O_5 as determined by XPS measurements. As for the first set of devices, for each MX_2/MO combination, an additional device was produced in which the metal dichalcogenide layer was annealed. The device structure is shown in Figure 6 (not to scale).

We found that the annealing of the metal dichalcogenide layer prior to plasma treatment, and the length of the plasma treatment affected the device performance. Selected I-V-L and power spectra are plotted in figures 7-12 (Figures 7 and 8 show the results for the niobium-based devices, Figures 9 and 10 show the results for the molybdenum-based devices, and Figures 11 and 12 show the results for the tantalum-based devices). Data derivable from these spectra are shown in Table 2 below.

Table 2

Material	annealing MX ₂ at 250°	Oxygen plasma min	Current density at 6V mA/cm ²	luminance at 6V cd/m ²	Power efficiency Lm/W	Emission efficiency cd/A
NbSe ₂	no	5	1400	23000 (31500 at 5.7V)	7.9 at 2.8V	7.8 at 3.4V
NbSe ₂	no	10	3300	24000 (30000 at 5.1V)	9 at 2.6V	7.6 at 2.6V
NbSe ₂	no	20	1200	27500	7.5 at 2.7V	7 at 3.2V
NbSe ₂	yes	5	500	24000	7.2 at 3.0V	7.5 at 3.7V
NbSe ₂	yes	10	2550	48000 saturated at 5.5V	6.8 at 2.8V	6.3 at 3.1V
NbSe ₂	yes	20	1100	20000	5.7 at 2.5V	8 at 2.5V
MoS ₂	no	1	750	31000	9.4 at 2.4V	8.4 at 2.7V

Material	annealing MX ₂ at 250°	Oxygen plasma min	Current density at 6V mA/cm ²	luminance at 6V cd/m ²	Power efficiency Lm/W	Emission efficiency cd/A
MoS ₂	no	5	2300	58000 saturated at 6.0 V	5.9 at 2.8V	5.4 at 2.8V
MoS ₂	no	10	3000	56000 saturated at 5.5 V	7 at 2.7V	6 at 2.7V
MoS ₂	no	20	1000	40000	7 at 2.4V	6 at 2.8
MoS ₂	yes	1	1600	40000 saturated at 5.6V	9.5 at 2.5V	7.5 at 2.5V
MoS ₂	yes	5	2000	50000 saturated at 5.7V	7.5 at 2.6V	6.5 at 2.6V
MoS ₂	yes	10	700	20000	10 at 2.6V	8 at 2.6V
MoS ₂	yes	20	1900	53000	9.5 at 2.4V	7.7 at 2.9V

Material	annealing MX ₂ at 250°	Oxygen plasma min	Current density at 6V mA/cm ²	luminance at 6V cd/m ²	Power efficiency Lm/W	Emission efficiency cd/A
TaS ₂	no	10	1400	23000 (31500 at 5.7V)	10 at 2.6V	1.5 at 2.8V
TaS ₂	yes	10	3300	24000 (30000 at 5.1V)	3.2 at 2.5V	4.5 at 3.3V
Control Device PEDOT			1400	61000	10.5 at 2.4V	9.4 at 2.9V

LED performance for the device structure with MX₂ as the hole transport layer and the corresponding metal oxide as an electron blocking layer

Despite the fact that the thickness of the injecting and blocking layers and the blend composition were not optimised, the devices can be seen from the above to exhibit very high light emission and power efficiencies. It is important to point out that no life-time and stability measurements have yet been done. However, since the metal chalcogenides and the corresponding metal oxides are stable at high temperatures (>750°C), it is expected that these devices will be reasonably stable and long-living.

In conclusion, the results above show that layered metal chalcogenides exhibit several important characteristics that make them highly promising materials for use as hole transport layers in organic electroluminescent devices:

- I. High work function
- II. Easy chemical (solution) processing

- III. Ability to form continuous ultra thin films
- IV. Simple conversion into the corresponding insulating oxide
- V. Stability at high temperatures.
- VI. Chemically inert.

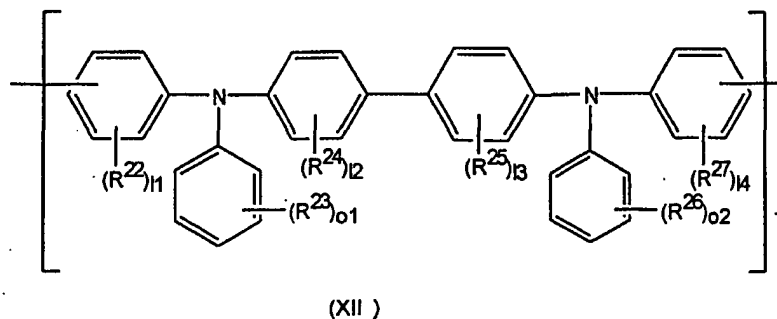
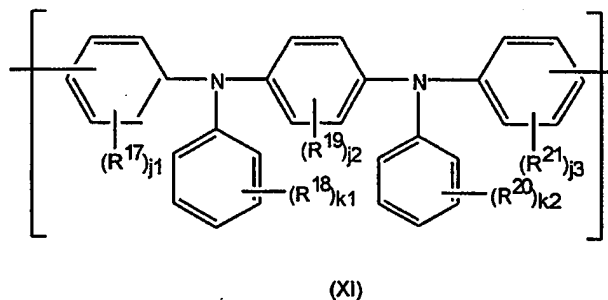
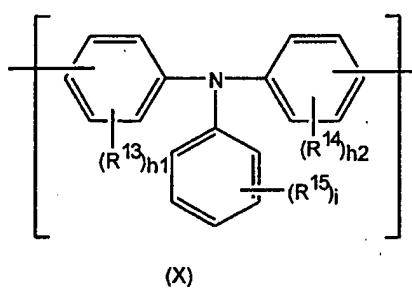
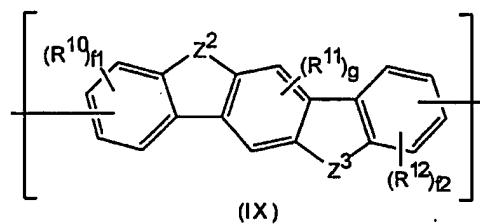
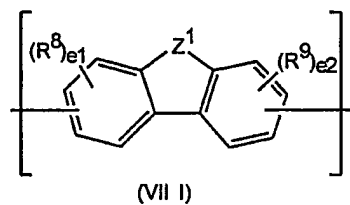
Claims

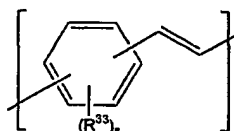
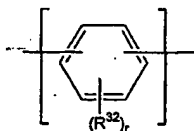
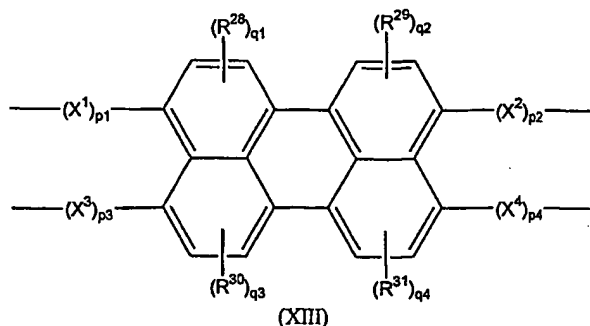
1. An electroluminescent device comprising a hole injecting electrode, an electron injecting electrode and at least one organic light emitting layer disposed between said hole injecting electrode and said electron injecting electrode, wherein a layered metal chalcogenide layer is disposed between said hole injecting electrode and said light emitting layer, the chalcogen component of said chalcogenide being chosen from sulfur, selenium and tellurium.
2. An electroluminescent device according to claim 1, wherein said layered metal chalcogenide is the only hole transporting material.
3. An electroluminescent device according to claim 1 or claim 2, wherein said layered metal chalcogenide has a work function of from 4 to 6.5 eV.
4. An electroluminescent device according to claim 1 or claim 2, wherein said layered metal chalcogenide has a work function of from 5 to 6.5 eV.
5. An electroluminescent device according to any one of claims 1 to 4, wherein said layered metal chalcogenide has a resistivity of from 1×10^{-4} to $10 \Omega\text{-cm}$.
6. An electroluminescent device according to claim 1, wherein said layered metal chalcogenide is a layered metal dichalcogenide.
7. An electroluminescent device according to claim 6, wherein the metallic component of said layered metal dichalcogenide is selected from the group consisting of titanium, zirconium, hafnium, vanadium, tantalum, niobium, molybdenum, tungsten and tin.

8. An electroluminescent device according to claim 6, wherein the metallic component of said layered metal dichalcogenide is selected from the group consisting of niobium, molybdenum, tantalum, tin and tungsten.
9. An electroluminescent device according to any one of claims 1, 2 and 6 to 8, wherein the chalcogen component of said layered metal chalcogenide is selected from the group consisting of sulfur and selenium.
10. An electroluminescent device according to claim 1 wherein said layered metal chalcogenide is selected from the group consisting of tantalum disulfide, molybdenum disulfide and niobium diselenide.
11. An electroluminescent device according to any one of claims 1 to 10, wherein said layered metal chalcogenide layer has a thickness of from 3 to 20 nm.
12. An electroluminescent device according to any one of claims 1 to 10, wherein said layered metal chalcogenide layer has a thickness of from 3 to 10 nm.
13. An electroluminescent device according to any one of claims 1 to 10, wherein said layered metal chalcogenide layer has a thickness of from 3 to 7 nm.
14. An electroluminescent device according to any one of claims 1 to 13, wherein said layered metal chalcogenide layer is annealed at a temperature of at least 100°C after deposition thereof on said hole injecting electrode.
15. An electroluminescent device according to any one of claims 1 to 14, wherein said organic light emitting layer comprises a layer or layers of one or more organic light emitting materials or a blend of organic light emitting materials, wherein said organic light emitting material or materials is selected from the group consisting of polyphenylene-vinylene (PPV) and derivatives thereof, polyfluorene and derivatives thereof, polynaphthylene and derivatives thereof, polyindeno fluorene and derivatives thereof,

polyphenanthrenyl and derivatives thereof, aluminium quinolinol (Alq_3) complexes, complexes of transition metals, lanthanides and actinides with organic ligands, and quinacridone, rubrene and styryl dyes.

16. An electroluminescent device according to any one of claims 1 to 15, said organic light emitting layer comprises a layer or layers of one or more organic light emitting materials or a blend of organic light emitting materials, wherein said organic light emitting material or materials is selected from the group consisting of aluminium quinolinol (Alq_3) complexes and light emitting conjugated polymeric materials, which can be homopolymers or can contain two or more different conjugated units, wherein said polymers comprise conjugated units selected from the following groups of formulae (VIII), (IX), (X), (XI), (XII), (XIII), (XIV) and (XV):





wherein:

each of R^8 to R^{15} and R^{17} to R^{33} is the same or different and is selected from the group consisting of alkyl groups as defined below, haloalkyl groups as defined below, alkoxy groups as defined below, alkoxyalkyl groups as defined below, aryl groups as defined below, aryloxy groups as defined below, aralkyl groups as defined below and groups of formula $-COR^{16}$ wherein R^{16} is selected from the group consisting of hydroxy groups, alkyl groups as defined below, haloalkyl groups as defined below, alkoxy groups as defined below, alkoxyalkyl groups as defined below, aryl groups as defined below, aryloxy groups as defined below, aralkyl groups as defined below, amino groups, alkylamino groups the alkyl moiety of which is as defined below, dialkylamino groups wherein each alkyl moiety is the same or different and is as defined below, aralkyloxy groups the aralkyl moiety of which is as defined below and haloalkoxy groups comprising an alkoxy group as defined below which is substituted with at least one halogen atom,

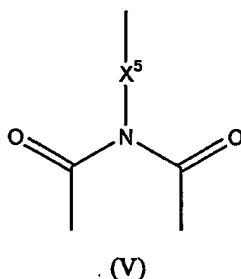
or, where r or s is an integer of 2, the 2 groups R^{32} or R^{33} respectively may, together with the ring carbon atoms to which they are attached, form a heterocyclic group having from 5 to 7 ring atoms, one or more of said ring atoms being a heteroatom selected from the group consisting of nitrogen, oxygen and sulfur atoms;

each of Z^1 , Z^2 and Z^3 is the same or different and is selected from the group consisting of O, S, SO, SO₂, NR³, N⁺(R^{3'})(R^{3''}), C(R⁴)(R⁵), Si(R⁴)(R⁵) and P(O)(OR⁶), wherein R³, R^{3'} and R^{3''} are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups as defined below, haloalkyl groups as defined below, alkoxy groups as defined below, alkoxyalkyl groups as defined below, aryl groups as defined below, aryloxy groups as defined below, aralkyl groups as defined below, and alkyl groups as defined below which are substituted with at least one group of formula -N⁺(R⁷)₃ wherein each group R⁷ is the same or different and is selected from the group consisting of hydrogen atoms, alkyl groups as defined below and aryl groups as defined below, R⁴, R⁵, R^{4'} and R^{5'} are the same or different and each is selected from the group consisting of hydrogen atoms, alkyl groups as defined below, haloalkyl groups as defined below, alkoxy groups as defined below, halogen atoms, nitro groups, cyano groups, alkoxyalkyl groups as defined below, aryl groups as defined below, aryloxy groups as defined below and aralkyl groups as defined below or R⁴ and R⁵ together with the carbon atom to which they are attached represent a carbonyl group, and R⁶ is selected from the group consisting of hydrogen atoms, alkyl groups as defined below, haloalkyl groups as defined below, alkoxyalkyl groups as defined below, aryl groups as defined below, aryloxy groups as defined below and aralkyl groups as defined below;

each of X¹, X², X³ and X⁴ is the same or different and is selected from:

arylene groups which are aromatic hydrocarbon groups having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted by at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined below, haloalkyl groups as defined below, alkoxyalkyl groups as defined below, aryloxy groups as defined below and alkoxy groups as defined below;

straight or branched-chain alkylene groups having from 1 to 6 carbon atoms;
 straight or branched-chain alkenylene groups having from 2 to 6 carbon atoms;
 and
 straight or branched-chain alkynylene groups having from 1 to 6 carbon atoms; or
 X^1 and X^2 together and/or X^3 and X^4 together can represent a linking group of
 formula (V) below:



wherein X^5 represents an arylene group which is an aromatic hydrocarbon group having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted by at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined below, haloalkyl groups as defined below, alkoxyalkyl groups as defined below, aryloxy groups as defined below and alkoxy groups as defined below;

each of e_1 , e_2 , f_1 and f_2 is the same or different and is 0 or an integer of 1 to 3;

each of g , q_1 , q_2 , q_3 and q_4 is the same or different and is 0, 1 or 2;

each of h_1 , h_2 , j_1 , j_2 , j_3 , l_1 , l_2 , l_3 , l_4 , r and s is the same or different and is 0 or an integer of 1 to 4;

each of i , k_1 , k_2 , o_1 and o_2 is the same or different and is 0 or an integer of 1 to 5; and

each of p_1 , p_2 , p_3 and p_4 is 0 or 1;

the alkyl groups above are straight or branched-chain alkyl groups having from 1 to 20 carbon atoms;

the haloalkyl groups above are alkyl groups as defined above which are substituted with at least one halogen atom;

the alkoxy groups above are straight or branched-chain alkoxy groups having from 1 to 20 carbon atoms;

the alkoxyalkyl groups above are alkyl groups as defined above which are substituted with at least one alkoxy group as defined above; and

the aryl group above and the aryl moiety of the aralkyl groups (which have from 1 to 20 carbon atoms in the alkyl moiety) and the aryloxy groups above is an aromatic hydrocarbon group having from 6 to 14 carbon atoms in one or more rings which may optionally be substituted with at least one substituent selected from the group consisting of nitro groups, cyano groups, amino groups, alkyl groups as defined above, haloalkyl groups as defined above, alkoxyalkyl groups as defined above and alkoxy groups as defined above.

17. An electroluminescent device according to any one of claims 1 to 14, wherein said organic light emitting layer is selected from the group consisting of PPV, poly(2-methoxy-5-(2'-ethyl)hexyloxyphenylene-vinylene) ("MEH-PPV"), dialkoxy and dialkyl derivatives of PPV, polyfluorene derivatives and related copolymers, and Alq3 complexes.

18. An electroluminescent device according to any one of claims 1 to 17, wherein a layer of a material is disposed between said organic light emitting layer and said layered metal chalcogenide hole transport layer which is capable of restraining migration of electrons from said organic light emitting layer to said layered metal chalcogenide hole transport layer.

19. An electroluminescent device according to claim 18, wherein said material which is capable of restraining migration of electrons from said organic light emitting

layer to said layered metal chalcogenide hole transport layer is an oxide of the same metal as that of said metal chalcogenide layer.

20. An electroluminescent device according to claim 19, wherein said layer of oxide of the same metal as that of said layered metal chalcogenide layer is formed by oxidising the exposed surface of the layer of the layered metal chalcogenide after it has been deposited on said hole injecting electrode.

21. An electroluminescent device according to claim 19 or claim 20, wherein said layer of oxide of the same metal as that of said layered metal chalcogenide layer has a thickness of from 1 to 10 nm.

22. An electroluminescent device according to claim 19 or claim 20, wherein said layer of oxide of the same metal as that of said layered metal chalcogenide layer has a thickness of from 2 to 6 nm.

23. An electroluminescent device according to claim 19 or claim 20, wherein said layer of oxide of the same metal as that of said layered metal chalcogenide layer has a thickness of from 2 to 3 nm.

24. An electroluminescent device according to any one of claims 1 to 23, wherein an electron transport layer is disposed between said electron injecting electrode and said organic light emitting layer.

25. An electroluminescent device according to claim 24, wherein said electron transport layer is selected from the group consisting of strontium oxide, magnesium oxide, calcium oxide, lithium oxide, rubidium oxide, potassium oxide, sodium oxide and cesium oxide.

26. An electroluminescent device according to any one of claims 1 to 25, wherein said hole injecting electrode is formed on a substrate selected from the group consisting of glass, quartz and crystalline substrates of Si, GaAs, ZnSe, ZnS, GaP and InP.
27. An electroluminescent device according to any one of claims 1 to 26, wherein said hole injecting electrode is formed from a material selected from the group consisting of tin-doped indium oxide (ITO), zinc-doped indium oxide (IZO), indium oxide, tin oxide and zinc oxide.
28. An electroluminescent device according to any one of claims 1 to 27, wherein said electron injecting electrode is formed a material selected from the group consisting of potassium, lithium, sodium, magnesium, lanthanum, cerium, calcium, strontium, barium, aluminium, silver, indium, tin, zinc and zirconium, and binary or ternary alloys containing said metals.
29. A process for the production of an electroluminescent device having a layered metal dichalcogenide layer according to any one of claims 6 to 28, which includes the step of depositing said layered metal dichalcogenide on said hole injecting electrode according to the following steps:
- (a) intercalation of lithium atoms into said metal dichalcogenide;
 - (b) addition of water to the resulting intercalated material resulting in an exfoliation reaction so as to give single layers of said metal dichalcogenide suspended in the water;
 - (c) addition of a water immiscible solvent to the product of step (b) followed by agitation of the resulting mixture to give a thin film of layered metal dichalcogenide at the solvent/water interface; and
 - (d) wetting said hole injecting layer supported on a substrate and then dipping it into the solvent/water interface produced in step (c) above and allowing the thin film of layered metal dichalcogenide to spread on the surface of said hole injecting layer.

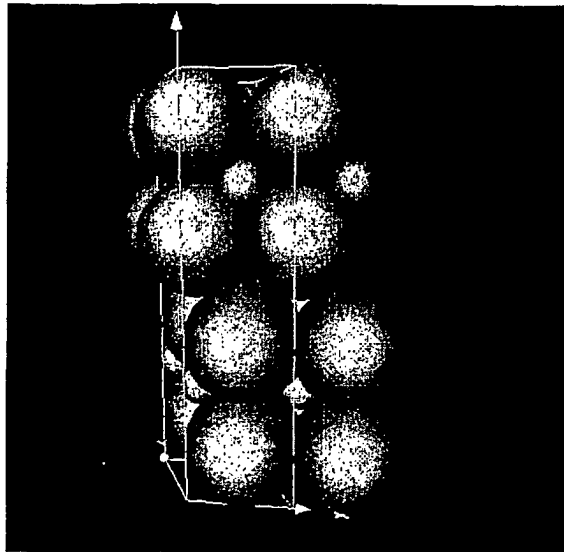


Figure 1

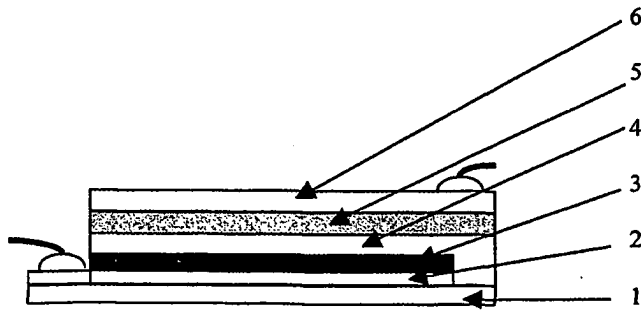


Figure 2

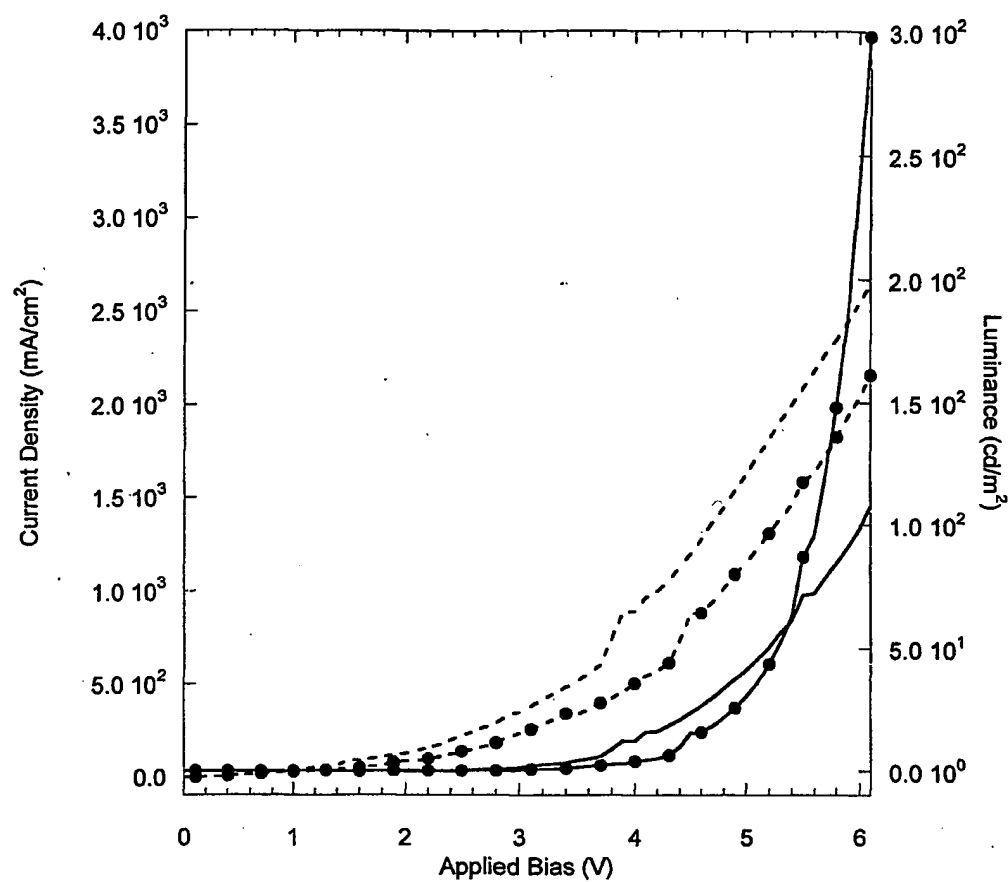


Figure 3:

J-V-L data for annealed (•) and unannealed (no marker)
 Glass/ITO/MoS₂/F8BT:TFB/Ca:Al Based Devices
 Current Density (dashed line), mA/cm²
 Luminance (solid line), cd/m²

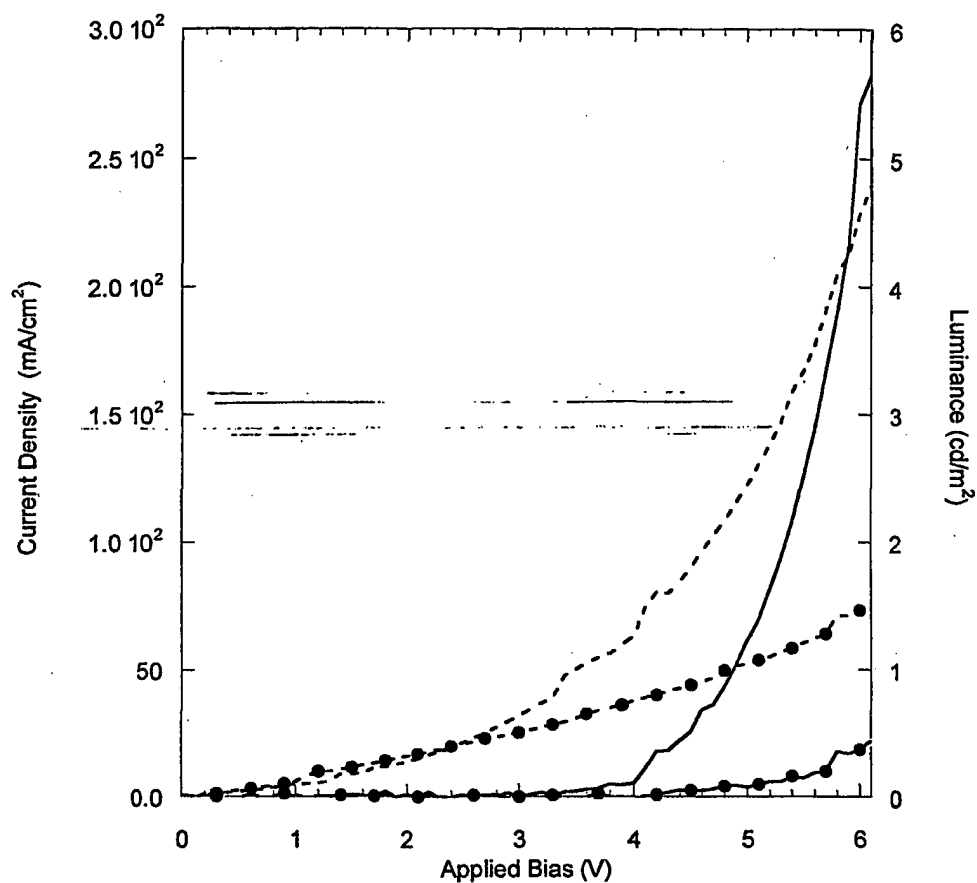
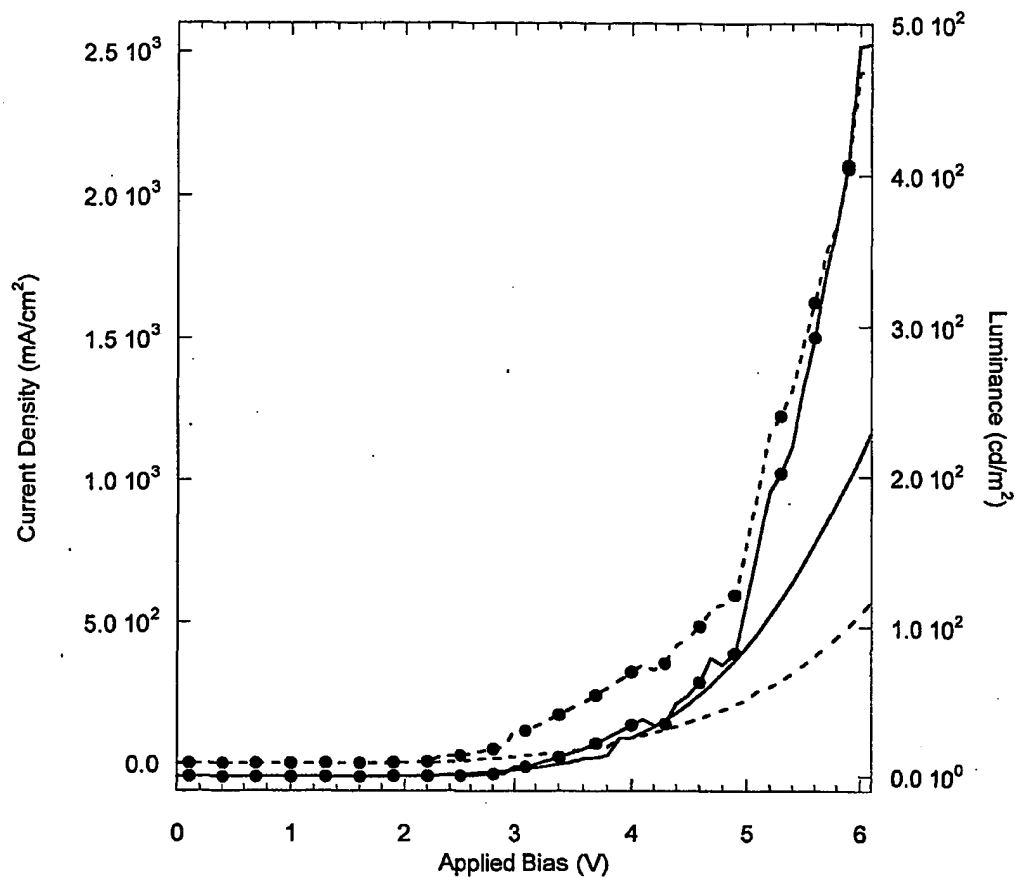


Figure 4

J-V-L data for annealed (•) and unannealed (no marker)
 Glass/ITO/TaS₂/F8BT:TFB/Ca:Al-Based-Devices
 Current Density (dashed line), mA/cm²
 Luminance (solid line), cd/m²

**Figure 5**

J-V-L data for annealed (•) and unannealed (no marker)
Glass/ITO/NbSe₂/F8BT:TFB/Ca:Al Based Devices
Current Density (dashed line), mA/cm²
Luminance (solid line), cd/m²

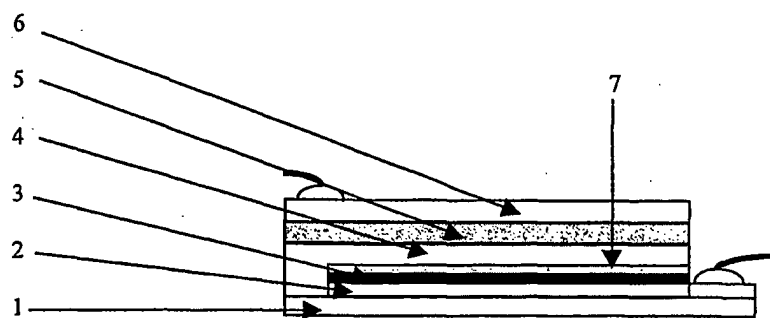


Figure 6

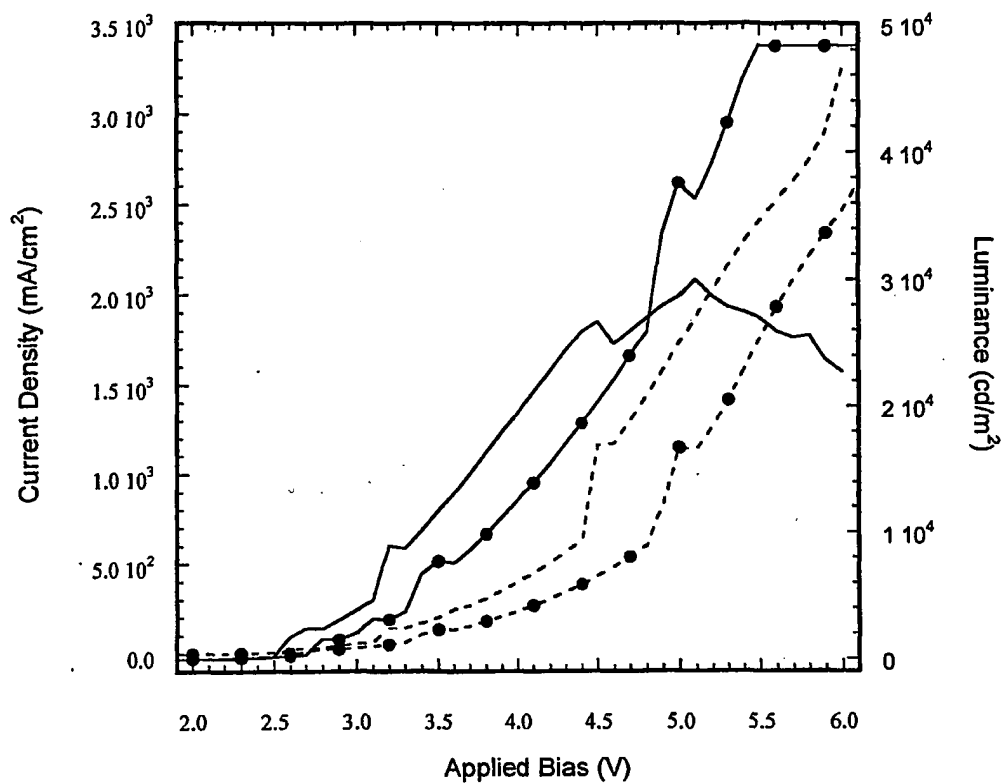


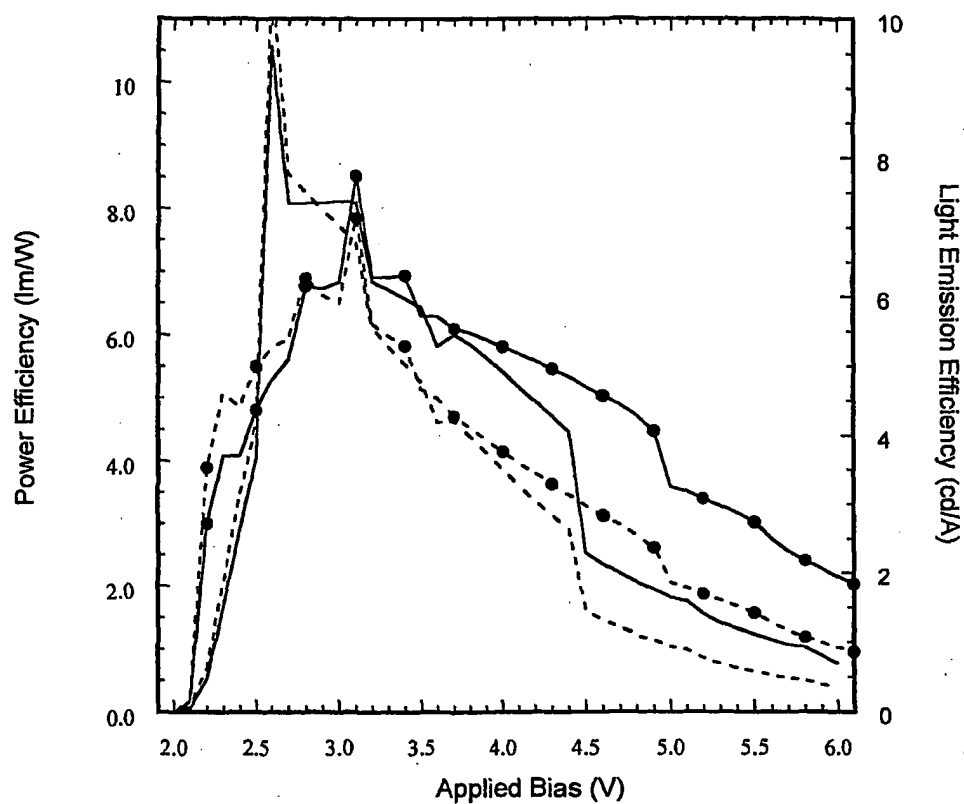
Figure 7

J-V-L data for annealed (•) and unannealed (no marker) Glass/ITO/NbSe₂/10 min O₂ plasma treatment at 250W/F8BT:TFB/Ca:Al Based Devices

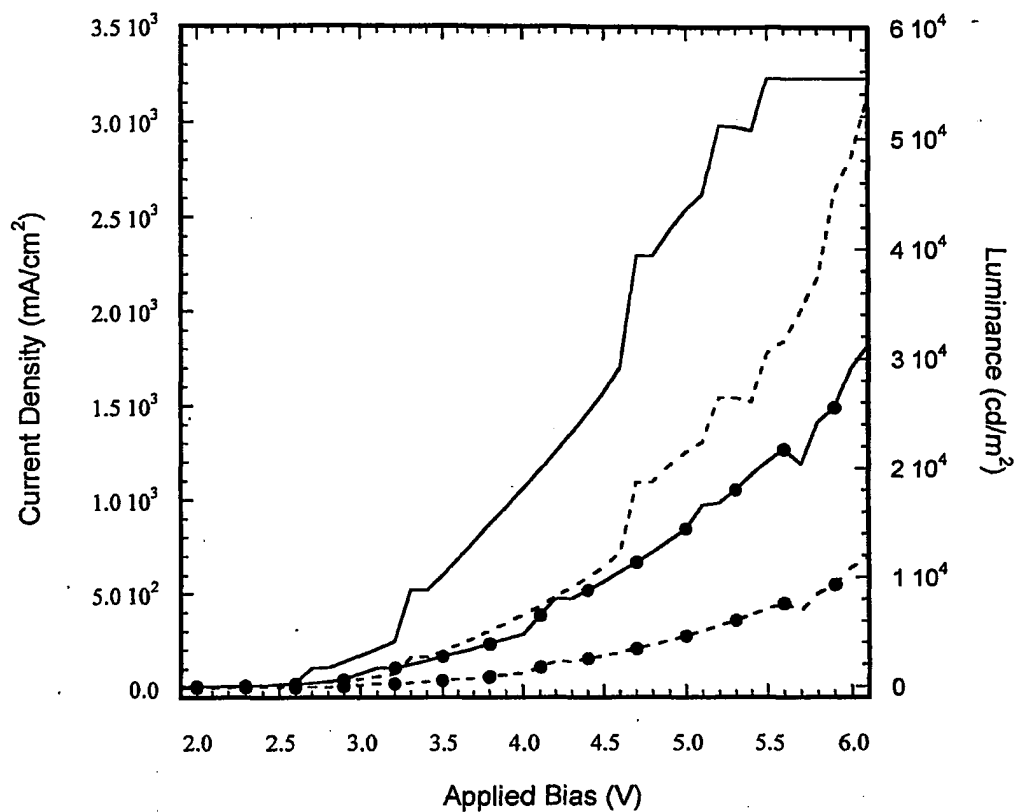
Current Density (dashed line), mA/cm²

Luminance (solid line), cd/m²

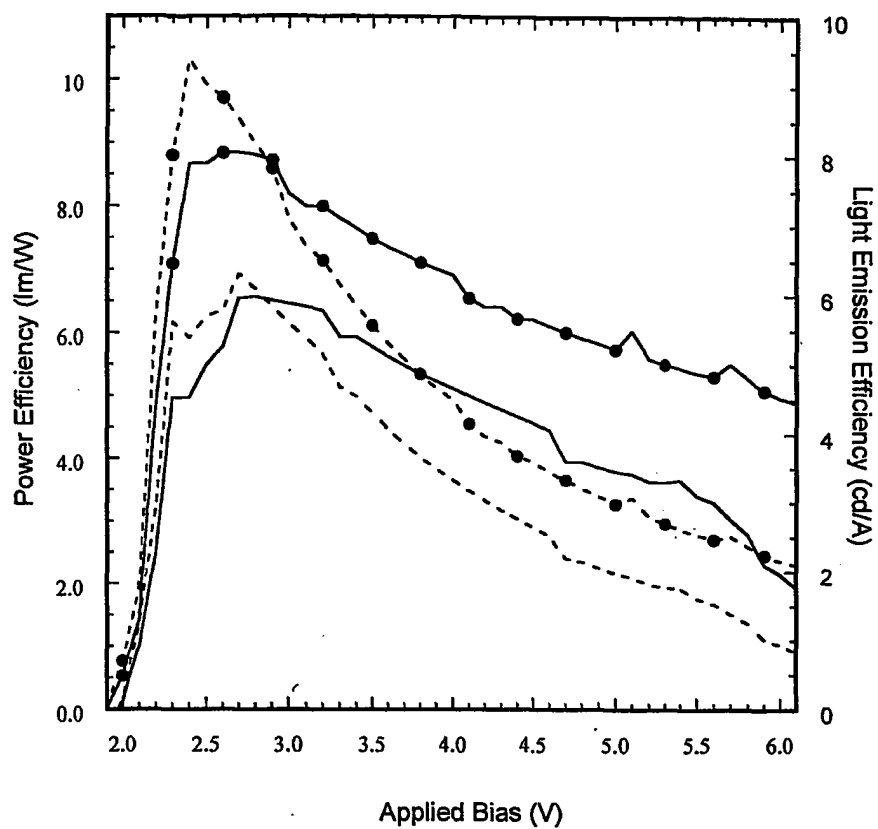
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**Figure 8**

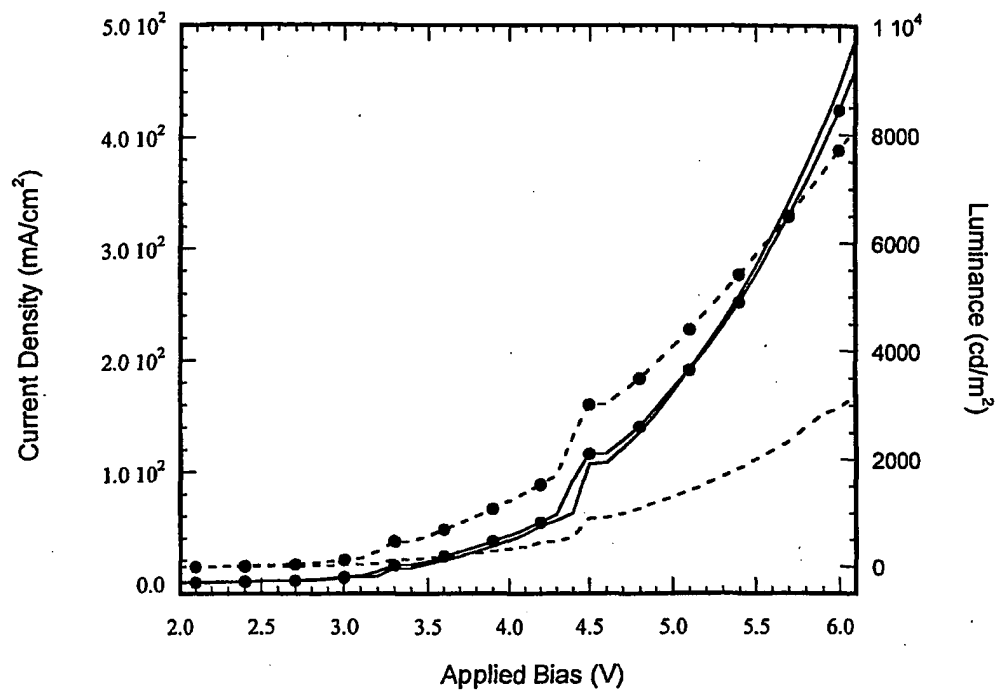
Efficiency data for annealed (•) and unannealed (no marker) Glass/ITO/NbSe₂/10 min O₂ plasma treatment at 250W/F8BT:TFB/Ca:Al Based Devices
Power Efficiency (dashed line), lm/W
Light Emission Efficiency (solid line), cd/A

**Figure 9**

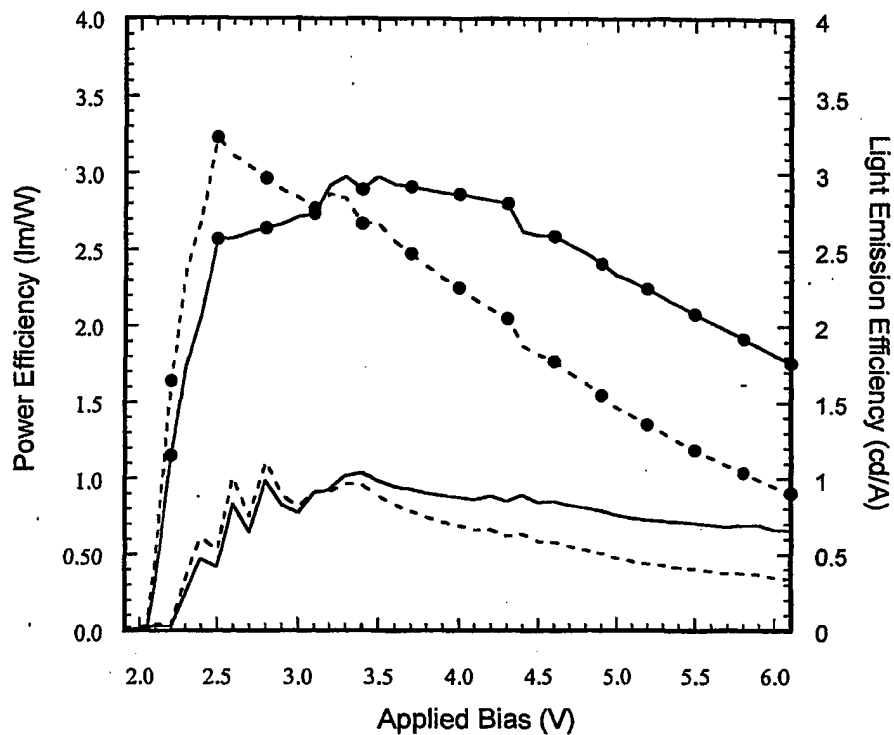
J-V-L data for annealed (•) and unannealed (no marker) Glass/ITO/MoS₂/10 min O₂ plasma treatment at 250W/F8BT:TFB/Ca:Al Based Devices
Current Density (dashed line), mA/cm²
Luminance (solid line), cd/m²

**Figure 10**

Efficiency data for annealed (•) and unannealed (no marker) Glass/ITO/MoS₂/10 min O₂ plasma treatment at 250W/F8BT:TFB/Ca:Al Based Devices
Power Efficiency (dashed line), lm/W
Light Emission Efficiency (solid line), cd/A

**Figure 11**

J-V-L data for annealed (•) and unannealed (no marker) Glass/ITO/TaS₂/10 min O₂ plasma treatment at 250W/F8BT:TFB/Ca:Al Based Devices
Current Density (dashed line), mA/cm²
Luminance (solid line), cd/m²

**Figure 12**

Efficiency data for annealed (•) and unannealed (no marker) Glass/ITO/TaS₂/10 min O₂ plasma treatment at 250W/F8BT:TFB/Ca:Al Based Devices
Power Efficiency (dashed line), lm/W
Light Emission Efficiency (solid line), cd/A

Novel polymers for light emitting diodes

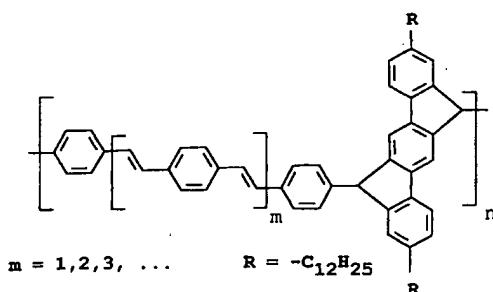
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We report a new polymer combining ladder type tri(*para*-phenylene) (LPP) and oligo(phenylenevinylene) (OPV) segments in an orthogonal arrangement. This polymer structure was designed to decrease the quenching processes of excitons by preventing the interchain aggregation of emissive units. The synthesis, absorption, solution and film photoluminescence as well as LED device performances of this new polymer are presented. Single layer LED devices showed blue emission with an external efficiency of 0.005%. Energy transfer from LPP to OPV was observed.

Ever since the first report of polymer light emitting diodes (PLEDs) in 1990 [1], the search for new polymers with stable and efficient electroluminescence properties has never faded [2–8]. Particular interest has been directed to the synthesis of blue-light-emitting polymers since blue light is usually hard to obtain in more conventional semiconductor LEDs. Generally, two approaches have been applied to obtain blue-light-emitting polymers. One is to synthesize polymers with wide bandgaps such as poly(*p*-phenylene)s (PPP) and its derivatives [9, 10], substituted poly(thiophene)s [11], poly(vinyl carbazole)s [12], etc.; the other is the utilization of limited conjugation segments, either in the polymer main chain [13, 14] or side chains [15–16].

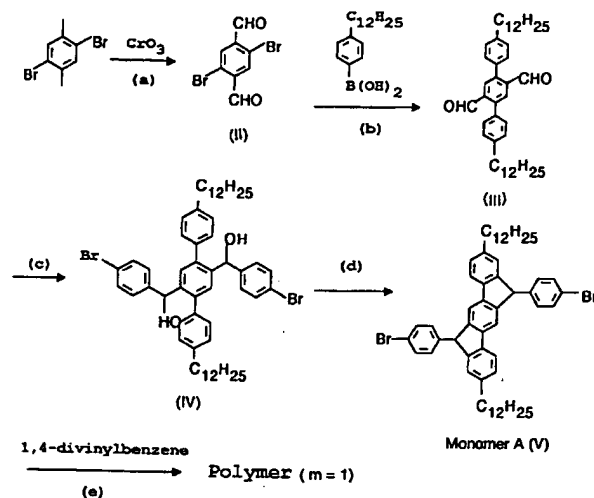
We report a novel polymer structure combining ladder-type tri(*para*-phenylene) (LPP) and oligo(phenylenevinylene) (OPV) segments in an orthogonal arrangement as shown in Scheme 1. Such an orthogonal structure was



Scheme 1. The structures of the polymers.

expected to decrease the quenching processes of excitons by preventing the aggregation of the OPV units, thus increasing the electroluminescence quantum efficiency and device stability [17]. Since the conjugation length of the OPV segment is defined and adjustable, the color of the emission can be easily controlled. For the polymer with three benzene rings and two double bonds as the OPV segment (Scheme 1, $m = 1$), we expect blue light to be emitted. Such a structure would also allow us to study the possible energy transfer from the LPP segment to the OPV unit. This communication reports the synthesis and the preliminary device demonstrations of this polymer.

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(a) CrO_3 , H_2SO_4 , AcOH , acetic anhydride then H_2SO_4 , EtOH , 40% overall yield.
(b) $\text{Pd}(\text{PPh}_3)_4$, Na_2CO_3 , toluene, 88% (c) 1,4-dibromobenzene, 1 eq. butyllithium, 93% (d) BF_3 , quantitative (e) $\text{Pd}(\text{OAc})_2$, $\text{P}(\text{o-tolyl})_3$, Et_3N , THF

Scheme 2. Synthesis of monomer A and the polymer.

The synthesis of the monomer and the polymer are shown in Scheme 2. 2,5-Dibromo-1,4-benzenedicarboxaldehyde (II) was synthesized in 40% yield by oxidation of 2,5-dibromo-*p*-xylene. The subsequent Suzuki reaction gives compound III in 88% yield [18]. It was found that the electron-withdrawing aldehyde group facilitates the Suzuki reaction. The reaction is complete in less than 6 h with excellent yield. Monolithiation of dibromobenzene and subsequent quenching by aldehyde (III) gave the desired product in 93% yield. Cyclization of compound IV gave monomer A (V) as a white needle crystal in quantitative yield [19].

Polymerization was carried out in typical Heck reaction conditions with THF as the solvent [20]. The polymerization was stopped usually after 5 h just prior to polymer precipitation from the solution. The molecular weight of the polymer ($M_n \sim 5600$, relative to the polystyrene standard), which was limited by its solubility, was rather low. However, high optical quality films could be spin-coated without any difficulty and the films remained clear over months.

Figure 1 shows the UV-vis absorption spectra of monomer A, and the polymer. For comparison, Fig. 1 also shows the UV-vis spectrum of a model compound, whose struc-

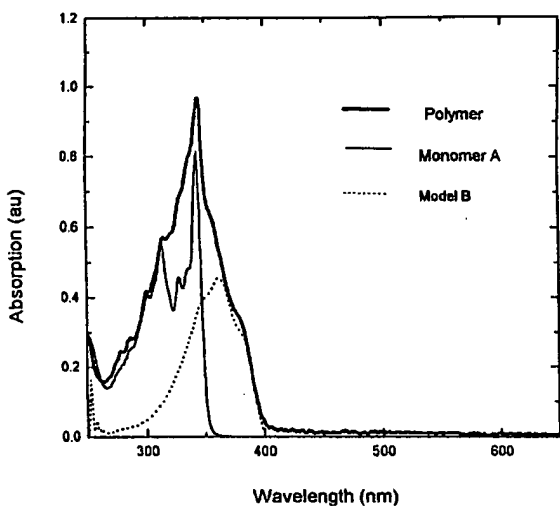
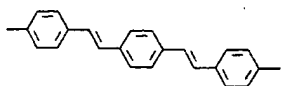


Fig. 1. UV-vis spectra of the polymer, monomer A, and model compound B.



Scheme 3. Structure of a model compound B.

ture is shown in Scheme 3. A steep onset at 3.55 eV for monomer A indicates its planar structure [21]. The absorption of the polymer shows the features of both OPV and LPP units. The absorption of the OPV unit partially overlaps with the absorption of the ladder LPP unit. The onset of the OPV unit, however, is at 3.11 eV, which is similar to that of model compound B but significantly larger than that of monomer A.

The fluorescence spectra of the polymer in solution and as a film show interesting results. As seen in Figure 2, the emission spectrum of monomer A has two peaks at 349 nm and 360 nm when excited at 340 nm in THF solution. These peaks can be ascribed to the LPP segment. When the polymer solution was excited at 340 nm, however, no or negligible emission from the LPP segment was observed. The polymer emission, which closely resembles that of model compound B shows three peaks in solution at 390 nm, 420 nm and 440 nm. Such results imply that the emission of the polymer predominantly comes from the PPV segment. Energy transfer from the LPP segment to the OPV unit clearly occurs. When the polymer film is excited at 337 nm, triple peaks are again observed with about 30 nm red-shift compared with that of the polymer solutions.

Single-layer LEDs using the polymer as the electroluminescent medium were fabricated. A thin polymer film was spin-cast (spin rate, 1000 rpm) from solution in tetrachloroethane (20 mg/2 ml) onto an indium-tin-oxide (ITO) coated glass substrate. A calcium electrode with thickness of ca. 500 Å was deposited on the polymer surface under vacuum at deposition rate of ca. 5 Å/s. The cal-

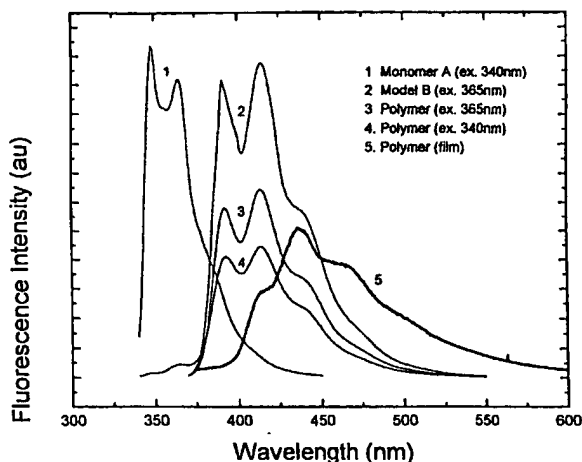


Fig. 2. Fluorescence spectra of the polymer, monomer A and model compound B in THF solution and as solid films.

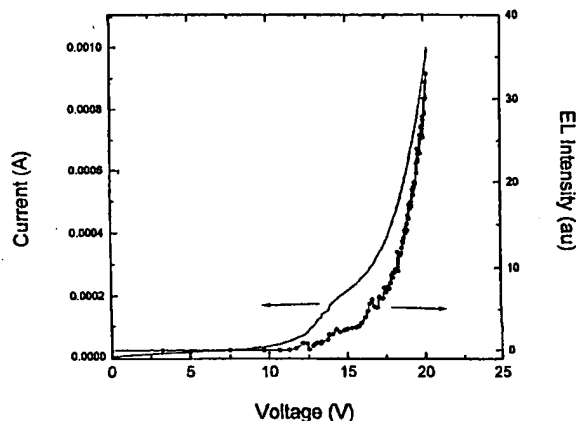


Fig. 3. Current-light-voltage characteristics of an (ITO/polymer/Ca) device.

cium electrode was then protected by covering it with a layer of silver via vacuum deposition. All other fabrication and testing steps were performed in air. Current-light-voltage characteristics of the devices were measured using a HP4155A Semiconductor Parameter Analyzer with a calibrated silicon photodiode detector. External quantum efficiencies were calculated as the ratio of photocurrent to electric current with a modification factor of 1.32 (correction factor of the detector sensitivity).

Blue light was observed for the single layer devices with calcium as the electrode. When aluminum was used as the cathode, no light emission was observed even at an applied voltage of 32 V. Figure 3 shows the typical current-light-voltage curves of this device. The light turns on at around 12 V. The brightness of the device was 6.6 cd/m² at current density of 1 mA/mm². The external quantum efficiency of this device was around 0.005%. Although such an efficiency is not great, which is believed due to the poor injection of electrons, it is certainly not bad either considering the simple

device configuration and comparing to the performance of polymers containing distyrylbenzene units [22].

Further work to increase the quantum efficiency by introducing oxadiazole into the PPV segment [23] and to control the color by changing the conjugation length of the PPV unit is in progress.

Experimental

2,5-dibromo-1,4-benzenedicarboxaldehyde (II): 70 ml of sulfuric acid was added dropwise into a suspension containing 20 g of 2,5-dibromo-*p*-xylene, 100 ml of acetic acid and 100 ml of acetic anhydride at 0°C. To the resulting mixture was added CrO₃ in portions so that the temperature of the mixture was no higher than 10°C. After stirring for half an hour, the greenish clear solution was poured into ice-water. The white solid was collected by filtration and washed with large amounts of water and methanol. The crude diacetate is pure enough for the next step. ¹H NMR (CDCl₃, ppm): δ 2.20 (s, 12H, —CH₃); 7.80 (s, 2H, —ArCH—), 7.88 (s, 2H, aromatic protons). The diacetate was hydrolyzed by refluxing it with a mixture of 100 ml of ethanol, 100 ml of water, and 10 ml of concentrated sulfuric acid for 2 h. The mixture was diluted with 200 ml of water and cooled. The product was collected by filtration and recrystallized from chloroform. (8.9 g, 40% overall yield, mp: 184–185°C). ¹H NMR (CDCl₃, ppm): δ 8.16 (s, 2H, aromatic protons), 10.34 (s, 2H, —CHO).

Compound III: A solution of compound II (2.30 g, 7.80 mmol), 4-dodecyl benzene boronic acid (4.83 g, 0.02 mol), Pd(PPh₃)₄ (0.44 g, 0.38 mmol), toluene (25 ml) and Na₂CO₃ (5 ml of 2M aqueous solution) was refluxed for 6 h under vigorous stirring. The mixture was poured into water and extracted with methylene chloride. The organic layer was washed with water, dried over MgSO₄ and the solvent was evaporated. The crude product was purified by chromatography (hexane:ethyl acetate = 10:1 as eluent) and further purified by recrystallization from chloroform/hexane. 4.3 g pure product was obtained as colorless plate crystals (88%, mp: 78–79°C). ¹H NMR (CDCl₃, ppm): δ 0.90 (t, *J* = 6.72 Hz, 6H, —CH₃), 1.29 (m, 36H, alkyl protons), 1.71 (m, 4H, alkyl protons), 2.70 (t, *J* = 7.69 Hz, 4H, benzyl protons), 7.34 (m, 8H, aromatic protons on the central phenyl ring), 8.10 (s, 2H, aromatic protons), 10.10 (s, 2H, —CHO). Anal. Calcd. for C₄₄H₆₂O₂: C, 84.83; H, 10.03. Found: C, 84.62; H, 9.76.

Compound IV: The BuLi (5.40 ml, 1.6 M solution in hexane, 8.64 mmol) in ether (10 ml) was added dropwise into a solution containing 1,4-dibromobenzene (2.03 g, 8.64 mmol) and 40 ml of anhydrous ether at 0°C. The resulting solution was stirred at room temperature for 1 h. To this solution was added dropwise a solution of compound III (2.00 g, 3.92 mmol) in ether (20 ml). A white solid precipitates out immediately. The resulting mixture was stirred for 15 min and then poured into water. The ether layer was washed with water and dried by MgSO₄. After evaporation of the solvent, the residue liquid was solidified from 200 ml of ligroin. The crude product was

collected by filtration and purified by recrystallization from chloroform/hexane to give 3.00 g of product as white powder (93%, mp: 122–123°C). ¹H NMR (CDCl₃, ppm): δ: 0.89 (t, *J* = 6.72 Hz, 6H, —CH₃), 1.26 (m, 32H, alkyl protons), 1.33 (m, 4H, alkyl protons), 1.68 (m, 4H, alkyl protons), 2.10 (s, 2H, —OH), 2.65 (t, *J* = 7.74 Hz, 4H, benzyl protons), 5.95 (t, *J* = 3.97 Hz, 2H, Ar₂CHO—), 7.01 (d, *J* = 8.40 Hz, 4H, aromatic protons), 7.15 (m, 8H, aromatic protons), 7.34 (d, *J* = 8.44 Hz, 4H, aromatic protons), 7.38 (s, 2H, aromatic protons). Anal. Calcd. for C₅₆H₇₂Br₂O₂: C, 71.78; H, 7.75. Found: C, 71.60; H, 7.63.

Monomer A: 1.93 g of BF₃ (13.60 mmol) was added dropwise to a solution of compound IV (0.57 g, 0.60 mmol, 100 ml methylene chloride). The resulting solution was stirred for five minutes at room temperature. Ethanol (10 ml) was then added, followed by 100 ml of water. The organic layer was washed with water, dried over MgSO₄ and the solvent was then evaporated. The crude product was recrystallized from CH₂Cl₂/MeOH to give monomer A as white needle crystals (mp: 186–187°C). ¹H NMR (CDCl₃, ppm): δ 0.87 (t, *J* = 6.73 Hz, 6H, —CH₃), 1.23–1.26 (m, 36H, alkyl protons), 1.55 (m, 4H, alkyl protons), 2.57 (t, *J* = 7.72 Hz, 4H, —ArCH₂—), 5.00 (s, 2H, CHAr₃), 7.03 (m, 6H, aromatic protons), 7.15 (d, *J* = 7.63 Hz, 2H, aromatic protons), 7.41 (d, *J* = 8.34 Hz, 4H, aromatic protons), 7.58 (d, *J* = 7.64 Hz, 4H, aromatic protons). Anal. Calcd. for C₅₆H₆₈Br₂: C, 74.65, H, 7.61; Br, 20.26. Found: C, 74.55; H, 7.51.

Polymerization: Typical Heck coupling conditions were used for the polymerization. ¹H NMR (CDCl₃, ppm): δ 0.87 (b, 6H, —CH₃), 1.23 (b, 36H, alkyl protons), 1.55 (b, 4H, alkyl protons), 2.57 (t, *J* = 7.72 Hz, 4H, —ArCH₂—), 5.00 (s, 2H, CHAr₃), 7.02–7.16 (m, 10H), 7.38–7.47 (m, 8H), 7.57–7.65 (m, 6H). Anal. Calcd. for C₅₈H₆₀: C, 92.01; H, 7.99. Found: C, 89.21; H, 6.99.

Acknowledgements

We thank Dr. M. Berggren for the photoluminescence measurement of the polymer films and Dr. E. A. Chandross, Dr. A. Dodabalapur for helpful discussions.

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Received January 30, 1998